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Volume 3

**ANALYTICAL CHEMISTRY OF THE
RARE EARTHS**

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ANALYTICAL CHEMISTRY OF THE RARE EARTHS

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MALIBU, CALIFORNIA

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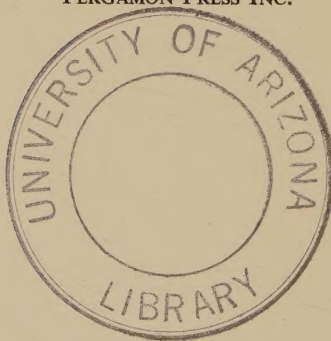
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PREFACE

THE custom once was for a modest author to preface his work with an apologia for weighting his readers down with another intellectual tome aimed at filling a 'felt want'. The present author would present a slight variant on this theme. Having worked in the rare earth field for many years, and having done his fair share of testing and rejecting methods of analysis, he was aware of the need for a monograph attempting to rationalize and stabilize analytical techniques as applied to the rare earths. The apology, therefore, is not for the work presented, but for the author's temerity in undertaking such a presentation when several other workers could undoubtedly have done a better job.

Generally, information on techniques of rare earth analysis is widespread — like the rare earths. But again, like the rare earths, this information occurs only sporadically in useful quantities. Schoeller and Powell, Meyer and Hauser, Hildebrand and Lundell, Scott, and the writer's *Chemistry of the Lanthanons* (now grossly archaic) all provide guideposts to procedures. The more definitive work is, however, too often tucked away like old theatre programmes, and requires overmuch effort and too much perusal and study of the literature before the bench bound analyst can undertake the task of analysing a sample sent in three weeks ago for 'determination and specification of rare earth content'. I have tried to collect and construe these data in one modest volume.

I have no doubt that the many laboratories now working with the rare earths will have developed specific techniques for specific analyses and may decry the absence of these techniques from this monograph. At this moment, however, I feel the requirement to be for a work covering the general field of rare earth analysis. Nevertheless, the hope resides that readers who have developed specific techniques will communicate them for possible inclusion in any subsequent editions.

My appreciation goes to Prof. Louis Gordon who suggested and convinced me that I should prepare this monograph — I would have

preferred it to emanate from his more able pen. I have been greatly aided moreover by encouragement, suggestions and recommendations from many of my past and present co-workers in this field, and most notably by my mentor, Dr J. K. Marsh of Oxford. To these and other chemists whose work, published and unpublished, has been a source of information — my deep appreciation. To my wife who typed the manuscript, and Pergamon Press who published it, my gratitude for having rendered legible my illegible scrawl.

But a final word of concern. Terminology has developed from an awkward word in a spelling bee to an International Conference on Nomenclature and, to avoid overmuch criticism from the pedantic semanticists, we must define our terms. Those used in this monograph, apart from the marginal comments, asterisks and calculations which undoubtedly and subsequently will appear, are those I suggested in *Chemistry and Industry* (London), June 26th, 1954. These may be conveniently summarized:

$$\text{La} + \text{Ce} + \text{Pr} + \text{Nd} + \text{Pm} + \text{Sm} + \text{Eu} + \text{Gd} + \text{Tb} + \text{Dy} + \text{Ho} + \text{Er} + \text{Tm} \\ + \text{Yb} + \text{Lu} = \text{lanthanons.}$$
$$\text{lanthanons} + \text{Y} + \text{Sc} = \text{Rare Earths.}$$

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CHAPTER I

HISTORICAL INTRODUCTION

THE FIRST rare earth to be discovered — yttrium — was isolated from gadolinite in 1794⁽¹⁾. One hundred and fifty years had to pass, however, before all members of the rare earth series had been separated and identified as entities. In retrospect, and knowing a little more about these elements, we may well be astonished that the early workers — Gadolin, Ekeberg, Mosander, Brauner, Urbain, von Welsbach, etc. — made such progress. Separation by prolonged and tedious processes of fractional crystallization, precipitation, etc., could be supplemented only by the crudest methods of detection and determination of individual rare earths. Confusion of description, terminology and even of individuality readily occurred because of this lack of analytic technique and instrumentation.

The earliest rare earth determinations involved, of course, identification via oxide or solution colour and equivalent weight. It was early realized that the rare earths could be precipitated almost *in toto* by oxalic acid from dilute mineral acid solution and that the insolubility of rare earth hydroxides would cause them to be found together with aluminium and iron in the third analytical group. Beyond this, the gravimetric techniques were essentially refinements of grosser scale separations, the usual analysis simply effecting separation of 'cerium' earths from 'yttrium' earths by precipitation of the double alkali sulphates⁽²⁾, under more or less standardized conditions.

'Redox' titrations of cerium were soon discovered and applied⁽³⁾ but this was apparently the early limit of individual determination. Curie's magnetic balance aided somewhat in following separation of elements, but so also did the simple equivalent, or average atomic, weight determination.

The difficulties of identifying individual rare earths were somewhat lessened when Gladstone first observed their absorption spectra in solution⁽⁴⁾, but, paradoxically, this new application of spectroscopy was more of a hindrance than a help in rare earth chemistry. The

multiplicity of, for example, the neodymium and praseodymium absorption spectra led to many arguments about the individuality of the elements, there arising, rather transitorily, the school which claimed 'one absorption band — one element⁽¹⁾'.

Apart from the early polynomial characterization of the rare earths, discrepancies and confusion arose because the early analysts too frequently were unaware of the valence state in which the element determined existed in the original material. Analyses for cerium, praseodymium and terbium, such as they were, were reported as the sesquioxides instead of the CeO_2 , Pr_6O_{11} , Tb_4O_7 , which had actually been determined. Despite the spectroscope and the magnetic balance, methods of purity determination were poor. A reasonably white product, resulting from fractional ammonia precipitation of a light lanthanon fraction, was totally considered to be lanthanum oxide with complete disregard for the 0.5–1 per cent of ceria which it probably contained. Even with cerium itself, authoritative statements of the colour of the oxide varied from 'pure white' through 'salmon pink' to 'tan'. It is now appreciated that the oxide colour is somewhat dependent upon its mode of preparation and particle size⁽⁵⁾. In gravimetry, colour of the oxide was the prime criterion and, in volumetric work the purity, or rather impurity, level of the standard was determinative.

In many instances, of course, errors cancelled out and it becomes a source of continued surprise, not that the earlier workers obtained any results at all, but that all too frequently the results of earlier mineral analyses are within one or two per cent of figures which we now smugly assume to have been rectified and developed to the n th degree of modern techniques. Apart from determinations of the purity of the separated products, much of the early analytical endeavour in rare earth studies emanated from attempts to understand the geochemistry of their mineral occurrences. Many of the previously believed correlations of rare earth contents with associated elements we now know to be immature and grossly incorrect. Since, in general, mineral association is largely dependent upon similarities in cation size, co-ordination number and ionization potential⁽⁶⁾ the most interesting and general associations of the rare earths are those involving titanium, the earth acids, uranium, and thorium. But it is separation from just these elements which produces the greatest inaccuracies in analyses as practised by the earlier chemists. An

interesting, if somewhat patronizing, exercise lies in the comparison of correlations given by Spencer⁽⁷⁾, Meyer and Hauser⁽⁸⁾ and Mellor⁽⁹⁾ with the more recent studies of Vainshtein *et al.*⁽¹⁰⁾, Ringwood⁽¹¹⁾, Murata *et al.*⁽¹²⁾, Wylie⁽¹³⁾ and Masuda⁽¹⁴⁾. But this is hardly germane to the present work and would serve essentially further to confirm the deductions of Goldschmidt and his co-workers⁽¹⁵⁾ and of Rankama and Sahama⁽¹⁶⁾. Appendix I summarizes what may be considered authenticated geochemical associations of the rare earths.

In many instances errors crept into older analyses because of the lack of appreciation of the naturalistic chemistry of the rare earths. We understand now, how Bergman⁽¹⁷⁾, d'Elhuyar⁽¹⁸⁾ and Scheele⁽¹⁾ missed the honour of the first discovery of the rare earths in Crondstedt's and Hisinger's minerals by mistaking them for lime. It is similarly easy to understand even those modern analyses which have failed to account adequately for scandium through non-appreciation of its amphoteric nature⁽¹⁹⁾.

As the uniqueness of rare earth absorption spectra became more appreciated and instrumentation improved, spectrophotometry was increasingly employed but errors were still encountered. The effects of anions and cations upon optical densities, extinction coefficients, and positions of the absorption bands were barely appreciated; some of the photographic techniques employed were only slightly more accurate than visual comparison of band intensities and of course the standards employed were frequently of dubious purity.

Analyses have not been consistently questionable, however. Between the two (so far) World Wars, our knowledge of the rare earths, and techniques for their analysis was extensively developed through the work of McCoy, James, Prandtl, Rolla, Marsh, Rodden, etc. But whenever gravimetric results were required (and this was frequently the case) or difference figures were inadmissible, recourse had to be made to the tedious fractional precipitation or crystallization procedures. Fraction checks of magnetic susceptibility, average atomic weight, or spectral absorption all played their part in determination of such elements as lanthanum, yttrium, gadolinium, etc., before results even slightly worthy of consideration could be obtained.

During this period analysis by emission spectrography underwent a major metamorphosis but only in the more recent years did standard rare earth materials of sufficient purity become available from which their emission spectra could be defined and tabulated correctly.

Even with this knowledge, the multifarious interferences occurring in the arc and spark still require much study and interpretation before satisfactory procedures can be established. The limitations and accuracy of these procedures will be dealt with subsequently.

The advent of the ion exchange era, propagated in England by Adams and Holmes⁽²⁰⁾ and nurtured through gestation, infancy and adolescence by workers on the Manhattan project⁽²¹⁾ abruptly changed the conditions under which workers in the rare earth field existed. Although now applied on industrial scales, the earliest ion exchange processes and techniques could have been considered almost exclusively analytical tools. Many modifications and improvements have been developed over the past fifteen years and, in a later chapter, we shall consider only the most refined applications of ion exchange to the analytical chemistry of rare earths.

In large scale separational processes, solvent extraction techniques are competing with ion exchange on a widening basis; analytically however, solvent extraction has been employed for many years in many ways. Nevertheless, in rare earth analysis our present knowledge somewhat seems to limit the application of this procedure.

Probably the most recently developed instrumental technique applicable to rare earth analysis has been that of X-ray spectrometry. Whilst emission spectrography still appears to present the final criterion for detection and determination of small amounts (p.p.m.) of rare earths, X-ray studies appear to be becoming increasingly applicable and applied to analysis for larger quantities by reason of their rapidity, versatility and accuracy in comparison with spectrophotometry.

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CHAPTER II

SAMPLE DECOMPOSITION

IN GENERAL, modes of attack of rare earth minerals and materials follow, on a more refined scale, those employed for decomposition of the mineral or ore before mass separation of the elements⁽¹⁾. Many coarse procedures which are, however, applied on a massive scale — such as chlorination — have not thus far been adapted, and do not seem easily adaptable, to analytical techniques.

Early studies of rare earth chemistry rapidly showed that no one method of sample decomposition could be employed satisfactorily upon all types of rare earth materials. In this respect the analyst ultimately will have to exercise his own judgment as to the most suitable acid or reagent according to the nature of the determination required. Since metathesis of rare earth compounds to hydroxide is readily accomplished by concentrated sodium hydroxide solution, and the hydroxides are readily soluble in acids, only very infrequently will it be found that the rare earths cannot be obtained in solutions of acid most appropriate to subsequent determinations. As will be indicated later, however, the use of strongly alkaline solutions must be undertaken with particular care when scandium is, or is believed to be, present.

Fine comminution of samples is, of course, a prerequisite, and no analyst should consider decomposition of a sample until it has been reduced in an agate mortar to a particle size of at least 200 mesh. Even when thus finely divided some material will resist attack; particularly is this so with some samarskites and other materials containing the earth acids. These should therefore preferably be ground to —325 mesh before cautiously attacking with hydrofluoric acid.

Table 2-1 indicates reagents most appropriate for decomposition of the commoner minerals and compounds of the rare earths, and, for ease of reference, consideration and application of the major decomposing reactants are now treated *seriatim*.

TABLE 2-1. REAGENTS FOR ORE DECOMPOSITION

H ₂ SO ₄ and/or KHSO ₄	HCl (with or without H ₂ O ₂)	HF (or H ₂ SO ₄ + NaF)
Monazite	Allanite	Samarskite
Cerite ✓	Gadolinite ✓	Euxenite
Xenotime	Thorite	Fergusonite
Yttrotitanite	Wiikite	Yttrotantalite
Thorianite	Cerite	Thortveitite
Wiikite	Orthite	Polycrase
Yttrocerite	Bastnaesite	Davidite
Davidite	Lanthanite	Bazzite
Bastnaesite	Carbonates	Pyrochlore
Bazzite	Oxalates	Aeschnyite
Carbonates	All oxides except Ce.	Yttrocrasite
Fluorides	Hydroxides	Risorite
Oxalates	Hellandite	
Oxides	Yttrotitanite	
Hydroxides	Kielhauite	
Samarskite	Yttrocerite	
Plumboniobite		
Risorite		

SULPHURIC ACID

The use of sulphuric acid for the 'cracking' of minerals has come down to us through the ages, and indeed some separational processes have been based upon its use. Because of the negative heats of solution and relatively low solubilities exhibited by the rare earth sulphates^(1, 2) however, it would seem preferable to retain the rare earths in association with some anion other than sulphate. This is usually effected by following the initial acid attack by a hydroxide metathesis and then redissolving the obtained hydroxides in e.g. hydrochloric or nitric acids.

Sulphuric acid (or alkali bisulphate — see below) is generally employed in working up cerite, monazite, xenotime, etc., the finely ground ore being heated to decomposition with twice its weight of acid. Actually only about a quarter of this weight of acid is really necessary, but the excess maintains the mass fluid enough to allow reaction to proceed as the sulphates crystallize from the heated mass. On attack of monazite or other ceriferous ores by sulphuric acid, the mass gradually develops an orange-red colour owing to the formation of ceric sulphate $\text{Ce}(\text{SO}_4)_2$ or the acid

sulphate $\text{CeH}(\text{SO}_4)$. Overheating causes reduction and dehydration to the white tervalent sulphate $\text{Ce}_2(\text{SO}_4)_3$; it should be avoided unless subsequent metathesis is intended. Solubilities of some octahydrated rare earth sulphates are shown in Table 2-2. Scandium solutions

TABLE 2-2. SOLUBILITIES OF OCTAHYDRATED SULPHATES (g/100 g H_2O)

	20°C	40°C
La	3.80	1.50
Ce	23.80	10.30
Pr	12.74	7.64
Nd	7.00	4.51
Sm	2.67	1.99
Eu	2.56	1.93
Gd	2.89	2.19
Tb	3.56	2.51
Dy	5.07	3.34
Ho	8.18	4.52
Er	16.00	6.53
Yb	34.78	22.90
Lu	47.27	16.93
Y	9.76	4.90
Sc	28.50	33.60

excepted, aqueous solutions of these sulphates, made in ice cold water, deposit crystals of one or more hydrates $\text{RE}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$ with increase in temperature. The normal solubility of scandium sulphate in comparison with the inverse solubility of the other rare earths with temperature is an interesting phenomenon⁽³⁾. From the data given, the recommendations of earlier workers that ice cold water be employed for sulphate dissolution can be well appreciated. This lack of solubility of the sulphates is a great disadvantage in the use of sulphuric acid for mineral decomposition — that is, unless very high acidities or dilution be employed. In determining cerium by redox titration it is necessary that high acidities and concentrations be maintained, else hydrolysis of the Ce^{4+} ion occurs, with consequent precipitation of ceric hydroxide and basic sulphate.

After attack by sulphuric acid, concomitant lead, barium, calcium, silica, etc., remain as residue, and the analyst must be careful to ensure that no rare earth sulphate is occluded or entrained with them. As a matter of general precaution it is probably advisable to consider

sulphuric acid (or alkali bisulphate for that matter) as merely a primary means of decomposition. Once mineral breakdown is effected, the sulphate, dissolved or not, should be converted to hydroxide. Sodium hydroxide pellets or concentrated solution may be added directly but cautiously to the diluted sulphate slurry. If solid caustic alkali be used, heats of hydration and reaction are usually quite sufficient to raise the temperature of the mass to boiling point, and metathesis is accomplished almost instantaneously. The resultant hydroxides of the rare earths, iron, calcium, etc., are thus obtained in a heavy, readily filterable condition. The characteristic colour changes which occur during this treatment are due to the formation first of cerous, then ceroso-ceric, and finally ceric hydroxides. After washing twice by decantation, with hot distilled water, filtration and further washing, the hydroxides can be redissolved in nitric, hydrochloric or perchloric acids, reprecipitated by ammonium hydroxide, and filtered free from all but the last traces of phosphate, sulphate, etc.

Titanium, tantalum, niobium, hafnium and zirconium divide between the mineral acid solution of the hydroxides and the various filtrates but are removed from the dilute acid solution of the hydroxides by boiling. There is rarely need to adjust the pH of the acid solution of the hydroxides, since the amount of acid required for redissolution is very nearly theoretical and the pH of the solution seldom drops below 3.5–4.0. At this acidity level titanium, tantalum, niobium, etc., readily hydrolyse. In the finest work, however, the hydrolysed precipitate should be reworked for any rare earths which possibly may have been occluded. The precipitate should be filtered through a pad of paper pulp, the filter and precipitate digested with hydrochloric acid, and the solution thus obtained diluted to about 5 per cent acidity. After boiling to ensure reprecipitation of the earth acids, etc., the solution is again filtered, when any occluded rare earths will pass through into the filtrate.

If the initial attack by sulphuric acid be taken to dehydration of the sulphates formed, silica present will also be dehydrated and remain unaffected upon caustic metathesis, thus appearing finally with the rare earth hydroxides. Hydrolysis of the final acid solution for elimination of titanium, etc., will remove some silica, but where no hydrolysable elements are present the final acid solution should be evaporated to dryness, baked, redissolved in a dilute acid, and filtered

free from the silica. Any silica entering the caustic solution and required for complete analysis may be recovered therefrom by normal means.

Procedure: Weigh 2 g of finely powdered monazite, xenotime, etc., into a 500 ml Phillips beaker. Moisten slightly with a few drops of water to avoid adherence of the ore to the beaker. Add 10 ml concentrated sulphuric acid, cover, and heat to SO_3 fumes until decomposition is complete (2–3 hr). Cool, first in air, then in an ice bath, and cautiously dilute with 100 ml distilled water. Stir gently to suspend the basic sulphate crystals and add cautiously 20 per cent sodium hydroxide solution or small sodium hydroxide pellets until the solution is alkaline (pH *ca.* 10). Boil for 10 min, then dilute to 400 ml with hot water. Allow to stand and wash the precipitated hydroxides three times by decantation with hot water. Finally, filter through a Whatman 541 paper and again wash twice with hot water. Return the precipitate to the original beaker and dissolve in the minimum of nitric acid, dilute to 50 ml, warm, and filter from unattacked zircon, rutile, etc.

BISULPHATE FUSION

Potassium bisulphate is usually recommended instead of the sodium salt for decomposition of rare earth minerals by bisulphate fusion. Not only are the minerals decomposed by this treatment, but double alkali sulphates are also formed and the sodium rare earth sulphates are, in general, less soluble than those of the potassium salt⁽⁴⁾. In practice, however, since subsequent hydroxide metathesis is again the preferred procedure, it would seem immaterial which alkali bisulphate be employed for the initial decomposition. Use of the potassium salt requires, however, a smaller excess of reagent than does the sodium salt, and far less reagent is generally required for bisulphate decomposition than in the sulphuric acid attack. An additional advantage of the fusion approach is, of course, the minimal amount of acid present in the final aqueous solution. The solid bisulphate cake obtained after mineral decomposition should be thoroughly disintegrated by boiling in water and aided by occasional light pressure from a glass stirring rod; the slurry obtained should be cooled somewhat before addition of solid sodium hydroxide. As has been indicated above, the colour change upon metathesis is interesting and clearly discernible when reasonable amounts of cerium are present. From the white-yellow sulphatic material the mass passes through grey, then purple phases indicating partial oxidation of the

cerium hydroxide produced. Under some circumstances, and particularly if the slurry be continuously boiled or allowed to stand and dry out over a night or weekend, further oxidation will occur, yielding the yellow ceric hydroxide.

Throughout any caustic metathesis, however, it must be remembered that, of the rare earths, any scandium present will largely pass into solution⁽⁵⁾. As will be emphasized subsequently, determination of scandium remains one of the most difficult problems in rare earth analysis. Scandium, it must be remembered, is amphoteric in nature and chameleon by intent. The possibility also exists that yttrium may exhibit some amphoteric characteristics⁽³⁾, and thus traces of this element must be sought for carefully in the alkali filtrate. Similar care must be observed in those instances in which high lanthanum contents are to be expected.

Aluminium, tin, and pentavalent chromium will also appear in the alkali filtrate and again must be sought for therein, or their presence at least noted as possible contaminants of any scandium in solution.

Procedure: Weigh 2 g of finely comminuted mineral, ore, etc., into a 50 ml platinum dish. Add about 5 g of potassium or sodium bisulphate and fuse gently over a Meker flame. As the initial frothing diminishes, increase the heating rate and swirl the melt gently to detach any crusts from the side of the crucible. Continue heating until decomposition is complete (10–15 min). Allow the crucible and contents to cool and solidify in a slanting position in order to render the solid cake more easily detachable from the crucible. When cool, add a few drops of water to the crucible and warm gently to detach the cake. Place the crucible and its contents in a 400 ml beaker, cover with 150 ml of 5 per cent sulphuric acid, and boil to disintegrate the cake. Aid the break-up of the mass by gentle attrition from the end of a glass rod and, when the mass is completely disintegrated, remove and wash the crucible in a stream of hot water. Pour the hot suspension of the melt (and washings) into an excess of hot 10 per cent sodium hydroxide solution. Allow the suspension of hydroxides to stand, then decant and treat as for the sulphuric acid treatment (above).

HYDROCHLORIC ACID

Allanite, gadolinite, bastnaesite, etc., are easily decomposed by hydrochloric acid; the acid may also be employed for the dissolution of carbonates, hydroxides, and oxide materials obtained as process products. The basic exception and rule on the use of hydrochloric

acid as a solvent of oxides lies with the cerium content. That oxides of high cerium content are resistant to hydrochloric acid attack has long been known, and Brauer and Hagg⁽⁶⁾ showed that the resistance to solubilization is essentially a function of the crystal structure of the oxide. Ceric oxide has an acid-resistant structure of the fluorite type, whereas the sesquioxides of the other rare earths adopt one or the other of the variations of the body centred cubic habit. Until 40 per cent cerium be present in the oxide mixture it is unable to impose its fluorite structure upon the cubic habit of the other rare earth oxides and is itself required to adopt the acid soluble cubic form. With cerium oxide contents above 40 per cent, however, the fluorite lattice predominates and the mixed oxides become increasingly resistant to attack by hydrochloric acid. When, therefore, more than 35 per cent of cerium is known, or expected, to be present in an oxide or mineral sample, hydrochloric acid should preferably not be employed. This criterion does not, of course, apply when carbonates, hydroxides, etc., are being considered.

At this point it may be remembered that boiling hydrochloric acid will decompose and dissolve the rare earth oxalates with the initial formation of oxalochlorides. Upon further digestion these decompose to the simple chlorides.

Because ceric chloride — CeCl_4 — is unknown and the hypothetical acid H_2CeCl_6 is very unstable, cerium in chloride solution may be considered to exist only in the trivalent state. Autoreduction similarly occurs when Pr^{4+} and Tb^{4+} oxides are dissolved in hydrochloric acid; in the case of these two elements, no valence states higher than 3+ have been found thus far in solution, regardless of the associated anion.

Mineral attack by hydrochloric acid will leave silica behind as a gelatinous residue, and dehydration by baking is then necessary to ensure its adequate removal from solution. In this process, dehydration of the rare earth chlorides will also occur together with the formation of the less soluble basic or oxychlorides. This can be avoided if dehydration be effected in a stream of hydrogen chloride, but under normal conditions a white, reluctantly soluble mass is obtained which has to be strongly treated to gain redissolution with dilute acid. Perseverance is here the keyword, and care should be taken to ensure that no rare earth chlorides remain with the insolubilized silica.

Commercial samples of rare earth chlorides are frequently submitted for analysis, and these too will contain silica. After dissolution in dilute (10 per cent) hydrochloric acid the solution of these should therefore be dehydrated and treated as indicated above for removal of this contaminant.

Where the oxide, mineral, or ore sample shows some reluctance to dissolve in hydrochloric acid alone, decomposition can usually be accelerated by the addition of nitric acid in small amounts, or more readily by the addition of hydrogen peroxide. The liberation of chlorine by such an attack readily decomposes all materials conventionally soluble in hydrochloric acid. It must be remembered also that, in the presence of the higher oxides of cerium, praseodymium and terbium, chlorine will be evolved as the oxides are dissolved and reduced. As will be indicated later, this presents one technique for determining the 'active oxygen' content of the oxide.

Procedure: Weigh 2 g of finely divided bastnaesite, oxide, etc., into a 250 ml beaker and add 50 ml of concentrated hydrochloric acid. Warm to near boiling and add dropwise 5 ml of 30 per cent hydrogen peroxide or concentrated nitric acid. Boil the solution until complete decomposition of the sample is obvious, making up the bulk of the acid, as it evaporates, with additional concentrated hydrochloric acid. Evaporate the solution to dryness and 'bake' for 20 min to dehydrate any silica present. Again take up the solid with 50 ml of concentrated hydrochloric acid and 5 ml of 30 per cent hydrogen peroxide. Boil to remove the peroxide from solution, cool somewhat, and filter through a Whatman 540 paper to remove silica, etc.

NITRIC ACID

Apart from its function in decomposing uraninite and davidite, nitric acid is but little employed in ore decomposition in either large-scale practice or in analysis. Thorianite may readily be decomposed by a mixture of nitric and sulphuric acids but, except for its application in dissolving hydroxide metathesis products, probably the greatest use of nitric acid as solvent lies in the attack of ceric oxide before gravimetric determination, or volumetric analysis after bismuthate oxidation. The effect of ceria content upon hydrochloric acid resistivity has been referred to above and, while this effect is still felt in nitric acid attack, it is generally avoidable by the judicious addition of hydrogen peroxide. When 'cerium oxides' are attacked

with nitric acid, the solution rapidly develops an orange-red colour owing to the presence of Ce^{4+} ions, but the attack of high-ceria materials slackens appreciably with time unless the ceric ions are reduced to the tervalent form. This is most readily accomplished by the addition of hydrogen peroxide. The red colour bleaches out and, when neodymium is present, its blue-pink colour becomes readily apparent.

When nitric acid – peroxide dissolution of the sample is to be followed by oxidative procedures for the volumetric determination of cerium, it is, of course, essential that all peroxide be removed from the solution by prolonged boiling, or more readily by the addition of e.g. ethanol or ferrous sulphate.

A prime value of nitric acid lies, however, not in initial decomposition of the ore, but in redissolution of the hydroxide material obtained upon caustic metathesis. From this point it is usual to precipitate the rare earths as group oxalates. If hydrochloric acid be the solvent during this reaction, the danger exists of precipitating, or at least occluding, oxalochlorides which, instead of igniting cleanly to the oxide, tend to result in a semi-fused oxychloride mass of indefinite composition. Redissolution of the hydroxides in sulphuric acid induces the formation of meagrely soluble sulphates or the precipitation of oxalosulphates. The oxalosulphates are converted completely to oxide only by ignition at relatively high temperatures, and the analyst has to be very careful to ensure complete decomposition of the intermediate sulphate. With nitric acid solutions none of these hazards exist, and the oxalates precipitated therefrom are readily ignited to oxides.

Procedure: Weigh 2 g of finely divided sample into a 250 ml beaker and slurry with a few drops of water. Add 30 ml of concentrated nitric acid and warm to initiate decomposition of the sample. Do not boil the solution but maintain at about 80°C . After about 5 min a red-orange colour develops. Add 30 per cent hydrogen peroxide dropwise to discharge this red colour and then five drops in excess. Repeat this reduction procedure as further development of red colour occurs and until the sample is completely decomposed. Evaporation losses of acid should be made up as necessary. After complete decomposition and reduction, dilute the solution to 100 ml, boil, and filter through a fine filter to remove traces of tin, etc., which may be present in the hydrolysed state.

HYDROFLUORIC ACID

Samarskite, euxenite and other earth-acid minerals containing the rare earths are normally decomposed by alkali bisulphate fusion (see above), by hydrofluoric acid, or by various mixtures containing both sulphate and fluoride anions. Where fluorides are used in large-scale practice, lead vessels are of course commonly employed. In analytical work one is able to revert to platinum ware. Attack by hydrofluoric acid is highly suitable for tantaloniobite ores of the rare earths, but it should be remembered that silica will always be lost when hydrofluoric acid is employed, and that aluminium fluoride also will volatilize unless sulphuric acid be present.

Although insoluble in hot water and in dilute mineral acid, the rare earth fluorides are perceptibly soluble in hot concentrated hydrochloric acid. Sulphuric acid converts them to sulphates with evolution of hydrogen fluoride. After initial acid attack and dehydration, however, it is preferable to digest the mass with 20 per cent caustic solution and thus metathese the fluorides to hydroxides. This treatment will bring into solution much of any associated tantalum or niobium, but these are not separated at this point. Instead the hydroxide product is dissolved in a minimum of dilute nitric or hydrochloric acid and boiled. Hydrolysis of the acid earths readily occurs and, after filtration, the rare earth solution is left free of such elements as tantalum, niobium, titanium, etc.

Procedure: Weigh 2 g of finely divided (325 mesh) sample (samarskite, etc.) into a 75 ml platinum basin and mix to a thin slurry with a few drops of 1 per cent sulphuric acid. Warm gently and add a few drops of nitric acid to ensure oxidation of any iron or uranium which may be present. Cool slightly and add concentrated hydrofluoric acid dropwise to the extent of about 15 ml. Warm again to initiate reaction and maintain this by the further dropwise addition of hydrofluoric acid and an occasional drop of nitric acid. The initially dark mass will gradually lighten in colour as the white, rare earth fluorides are produced and, when no more unattacked black particles are visible in the slurry, increase heating until the mass is completely dehydrated. It should be unnecessary to emphasise that these operations must be conducted under a good fume hood.

After dehydration, cool the crucible and contents and place in a 400 ml beaker. Cover with 150 ml of 20 per cent sodium hydroxide solution and boil to detach the fluorides from the crucible and convert them to hydroxides. After completion of metathesis, remove the crucible from the beaker and wash with hot water. Dilute the suspension to 300 ml with water and allow to stand. Decant the supernatant liquor and proceed as in sulphuric acid attack (above).

PERCHLORIC ACID

Very little reference is made in the literature to the use of perchloric acid for the decomposition of rare earth ores. The value of this acid in later stages — dehydration of silica, preparation of solutions for spectrophotometric analysis — appears well enough appreciated, but its application to initial attack would seem to be a virtually unexplored field. Gordon *et al.*⁽⁷⁾ have found monazite sand to dissolve rapidly in boiling 70 per cent perchloric acid, the formation of a yellow precipitate (probably ceric phosphate) beginning shortly after boiling. On cooling and diluting the solution, a yellow gelatinous precipitate of basic ceric phosphate forms. This can apparently be reduced and obtained in solution by the addition of hydrogen peroxide or hydrazine hydrochloride.

Nothing appears to be known about the decomposition by perchloric acid of siliceous or tantaloniobite rare earth minerals, but it might be expected that decomposition processes would be as in the case of monazite. The rare earth perchlorates are quite soluble in water and, while the effect of perchlorate anions upon the redox titration of cerium is not known, they cannot be expected to introduce errors of high magnitude.

Procedure (after Gordon, *loc. cit.*): Weigh 1 g of finely ground monazite sand into a 250 ml Erlenmeyer flask. Add 5 ml concentrated nitric acid and 30 ml 70 per cent perchloric acid, bring to gentle boiling, and continue for 1 to 1½ hr after initial evolution of dense white fumes of perchloric acid. Do not cover the flask during this decomposition.

Cool and add 15 ml water then 5 ml of 3 per cent hydrogen peroxide or 0.5 g hydrazine dihydrochloride. Warm for a few moments to clarify the solution and drive off gaseous reaction products. If the bulk of the gelatinous mass of phosphates does not redissolve, add 5 to 10 ml of concentrated hydrochloric acid. Cool the solution and filter to remove any unattacked residue of zircon, quartz, rutile, etc.

ALKALI FUSION

Use of caustic metathesis to obtain the rare earths as hydroxides from bisulphate or acid attack has been referred to above, but we have thus far not considered the direct use of alkali carbonate or hydroxide as media for fusion attack of rare earth ores.

Phosphates and silicates yield readily to fusion with ten times their weight of sodium-potassium carbonate, and the product rare earth

carbonates are readily obtained in solution with dilute acid. On fusion some lanthanum, lutetium, yttrium, and much scandium will form soluble alkali salts, and upon simple aqueous leach some will appear in solution. The other rare earths will remain as insoluble simple or complex carbonates.

Ore decomposition by this means must, of course, be effected in platinum vessels, but 'pick-up' of platinum under carbonate fusion is less than with bisulphate attack. Nevertheless, the final acid solution should be freed of any heavy metals and platinum by treatment with H_2S .

Fusion with sodium hydroxide and nitrate is a satisfactory method for the decomposition of phosphates, silicates and some earth-acid ores, but in such cases a silver crucible is to be preferred. Care should be taken not to melt the crucible and also to ensure removal of dissolved silver by subsequent treatment with hydrochloric acid and /or H_2S .

Use of sodium peroxide for fusion attack of rare earth minerals is unwise. Nickel or silver crucibles are thuswise required, and the introduction of impurities is at a high level. Removal of rare earths by oxalate precipitation from a solution containing high concentrations of nickel invariably leads to the entrainment of the heavy metal, so that repeated reprecipitation is necessary with its attendant losses in the prime precipitate.

Procedure: Weigh 1 g of finely divided monazite, cerite, etc., into a 50 ml platinum crucible. Add about 15 g of fusion mixture (sodium-potassium carbonates) and mix the two solids with the end of a glass rod. Fuse gently at first and then to the melting point of the carbonates, with occasional swirling to speed the attack. Allow fusion to proceed until complete decomposition is obtained. Cool the crucible and contents and leach with boiling water. When the fusion cake has been completely detached from the crucible, remove the crucible after washing with hot water and cautiously acidify the solution with hydrochloric acid. Boil gently to remove carbon dioxide and pass hydrogen sulphide to precipitate any dissolved platinum from solution. Filter off any sulphide precipitate together with any undissolved gangue, silica, etc. Boil the filtrate free of H_2S and dilute to volume in a graduated flask for further treatment.

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CHAPTER III

QUALITATIVE DETECTION

THE QUANTITATIVE determination of rare earths by chemical and spectral methods will be considered in subsequent chapters. Here we shall be considered only with those techniques applicable to primary detection of these elements. It must at all times be realized, however, that quantitative methods *per se* may be applied for detection purposes and that qualitative tests are, if of any value, precursors of quantitative procedures. In colour development techniques, for example, use of the spectrophotometer for determination of the wavelength of absorption can be followed immediately by determination of optical density at the wavelength of maximum absorption. Consequently the colouring element present can be determined quantitatively. To iterate therefore we shall be here concerned with procedures, or techniques which will reveal the presence of the rare earths either singly or together, without specific consideration of quantitative evaluation.

Although Martini⁽¹⁾ considered succinate precipitation to be the most sensitive technique for rare earth detection (*ca.* 1 γ) from the 'wet' chemistry standpoint, the most characteristic reaction of the rare earths, as a group, is the relative insolubility of their simple oxalates in dilute mineral acids. The limitations of this precipitation reaction must, however, be recognized. Solubilities of rare earth oxalates differ markedly with the rare earth cation species and its initially associated anion species, acid concentration, temperature and the presence of other cations and anions. Ammonium and carboxylate ions grossly affect solubility data whilst, as a corollary, concentration of the rare earths is probably the major factor influencing their detection by simple precipitation techniques. The precipitation of 'trace' concentrations (1 mg or less per 100 ml) of the rare earths by oxalate precipitation cannot be effected unless a 'carrier' element be present. As a general rule, calcium ions are extremely effective in this respect, although unless much calcium be present precipitation

will have to be carried out in alkaline solution. In acid solution (*ca.* pH 4) a calcium concentration of about 100 g/l. is necessary before precipitation by oxalate can occur. The value of calcium as a 'carrier' in oxalate solution has been well demonstrated by Lux⁽²⁾, Borneman-Starynekevich *et al.*⁽³⁾ and Robinson⁽⁴⁾.

Korenman⁽⁵⁾ reports solubility products for lanthanum, cerium and praseodymium oxalates in 0.1 N HCl at 20°C as 1.07×10^{-28} , 1.10×10^{-28} , and 1.3×10^{-28} respectively. These values increase in sulphate solution because of complex formation. The slight increase observable in these first three members of the lanthanon series is accentuated with progression through towards lutetium; the solubility product of yttrium oxalate lies between those of lutetium and scandium, the latter oxalate being the most soluble of the rare earth group⁽⁶⁾. Feibush *et al.*⁽⁷⁾ have recently determined the solubility product for yttrium oxalate as 5.34×10^{-29} , in reasonable agreement with the writer's unpublished value of 5.45×10^{-29} .

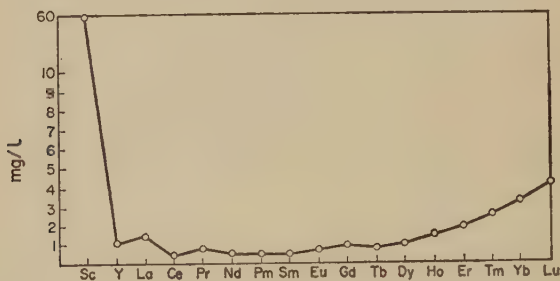


FIG. 3-1. Solubilities of hydrated rare earth oxalates in water at 25°C.

Figure 3-1 shows solubility data for the hydrated rare earth oxalates at 20°C, but in considering the data thus presented it must be remembered that these solubilities have been determined and recorded upon previously prepared oxalates; as the writer has shown⁽⁸⁾ particularly with scandium, under conditions of direct precipitation, supersaturation inevitably occurs so that the concentrations at which rare earths are detectable by oxalate precipitation are usually about twice those which might be expected by direct dissolution techniques. Studies on the solubility of scandium oxalate would appear to be somewhat vitiated by the development of hydrolyzed species. Thus the solubility of scandium oxalate in pure water can be found to be about 4.2×10^{-4} moles per litre but the solubility

figure invariably decreases when the moist salt is equilibrated with fresh quantities of water⁽⁹⁾.

Excess aqueous oxalic acid sparingly dissolves rare earth oxalates and reduces their solubilities in mineral acid, this depressant effect appearing to be greater in the heavier lanthanon group than in the lighter⁽¹⁰⁾. The simple oxalates precipitated from dilute acid change in characteristics with increase in mineral acid concentration, the solid phase becoming mixed, e.g. as in oxalochlorides or oxalosulphates.

The addition of oxalic acid to a solution containing Ce^{4+} ions reduces these to the tervalent state, no ceric oxalate being known. Upon ignition, rare earth oxalates ultimately decompose to oxides via the intermediate formation of basic and simple carbonates. Complete conversion to oxide requires a temperature of $800^{\circ}C$ for 30–40 min although the hydrate water is eliminated between 45 and 400° ⁽¹¹⁾.

Alkali oxalates also precipitate rare earth oxalates from mineral acid solution, but their use in analytical chemistry is generally to be avoided. Occlusion of alien elements increases when alkali oxalates are employed as precipitants, whilst alkali double oxalates are also formed which introduce alkalies into the precipitate which produce difficulties upon subsequent ignition. Ammonium oxalate and its rare earth double salts do not evince this troublesome ignition feature but the ammonium salt has a greater tendency than either the sodium or potassium oxalates to form soluble oxalato-complexes with the rare earths. Particularly should ammonium salts be avoided when scandium or yttrium are being sought by precipitation of oxalates⁽⁶⁾.

Precipitation of oxalates from homogeneous solution is probably best suited to quantitative determinations on conservative systems and will be considered in this context in a later chapter. In an unknown solution, examination for rare earths by oxalate precipitation is best conducted conventionally, with employment of double precipitation to ensure that precipitation of calcium (when in large concentrations) does not obscure that of the rare earths. Such a phenomenon readily occurs even at relatively high acid concentrations⁽⁶⁾.

Before employing oxalic acid as a group precipitant for the rare earths, it is best to ensure that iron, if present, is in the reduced state. The reducing effect of oxalic acid upon ceric irons has been noted

above but, in a solution containing Fe^{3+} ions the addition of oxalic acid leads to only partial reduction, an Fe^{3+} – Fe^{2+} equilibrium apparently being established leading to the precipitation of a ferroso-ferric oxalate. Ferrous oxalate is normally soluble in acids but excess oxalic acid depresses this solubility so that unless appropriate precautions are taken, iron will contaminate the rare earth oxalate precipitate. Soluble rare earth–iron oxalate complexes also form and, when large amounts of iron are present, precipitation can be expected to be incomplete. Uranyl salts have a similar inhibitory action upon rare earth precipitation⁽¹²⁾. Dutt⁽¹³⁾ claimed that the rare earths can be separated quantitatively from uranium only when the ratio $\text{U} : \text{Ln} < 25$. The reported work was incomplete however, since no indications were given of the concentration of the solutions employed nor of the excess (if any) of oxalic acid used. The author has found in unpublished spectrophotometric studies that, unless a great excess of oxalic acid be employed, rare earth precipitation is incomplete when uranyl or ferrous ions are present in apparent molar percentages greater than 60 and 50 per cent respectively.

The solubilizing effect of carboxylate ions upon rare earth oxalates has in general been exemplified only by those studies involving citrate, nitrilotriacetate, and ethylenediamine tetraacetate ions. In the case of the two latter, this solubilizing effect has been employed separationally⁽¹⁴⁾. But simpler carboxylates, such as acetates, have also a profound effect and can indeed prohibit precipitation; particularly is this so when the heavier lanthanons and scandium and yttrium are being specifically considered. If, therefore, carboxylate ions, or for that matter any organic anions are suspected in a rare earth solution, they should be removed by nitric acid digestion to dryness before attempting to detect the rare earths by oxalate precipitation.

Dutt (*loc. cit.*) found fluoride precipitation of the rare earths to give good recoveries, but it must be conceded that such precipitation is hardly specific. Additionally one must consider the great possibilities which exist for the development of soluble fluoride complexes⁽¹⁵⁾. The value of e.g. lanthanum fluoride as a carrier for the trans-uranium elements is now well known⁽¹⁶⁾, but less appreciated and less studied is the extent to which other, more common, elements are carried down, or conversely, the extent to which traces of the rare earths may be occluded in fluoride precipitates of other metals.

According to Sandell⁽¹⁷⁾ strontium fluoride may be expected to be a better 'collector' for lanthanum than is calcium fluoride. In view of the ready solubility of rare earth fluorides in 0.5 M aluminium nitrate solutions⁽¹⁸⁾ it is to be expected that attempts to precipitate the rare earths as fluorides from solutions of high aluminium content are likely to be less than successful. The stringency of pH control (2-2.5) must further be considered.

Although rare earth fluorides are in general to be considered very insoluble, except as noted above, their precipitation as such can hardly be considered specific. In pure rare earth solutions such precipitation can be taken as quantitative, but much endeavour has to be applied in attaining this status. Next to oxalate precipitation, probably the most specific reaction for determining the presence of the rare earths lies in their precipitation as double salts with sodium or potassium sulphate. Although probably the most generally employed in separation of the rare earths, this mode of precipitation is not so useful for their complete precipitation. Nevertheless it is a preferable technique when tentatively examining highly ferruginous solutions for light lanthanon content. Sodium, potassium, ammonium, or thallium sulphates may be employed as precipitants and although the chemistry of the precipitated double sulphates is still somewhat obscure, their composition may be summarized as $x\text{RE}(\text{SO}_4)_3, y\text{M}_2\text{SO}_4 \cdot z\text{H}_2\text{O}$ ⁽¹⁹⁾. The precipitate formed from solutions low in M_2SO_4 is very often $x = 1, y = 1, z = 2$ although the ratio y/z can vary from 1-6. As temperatures rise solubilities fall.

Solubilities of the double sulphates in water are generally quite low (Fig. 3-2) but, since an excess of precipitant will inevitably be present, differential solubility effects have to be considered. Early chemists readily observed that the rare earths can be divided into three groups according to the solubilities of their double potassium sulphates in a saturated solution of potassium sulphate namely:

soluble: yttrium, erbium, ytterbium, thulium, holmium and dysprosium;

slightly soluble: gadolinium, terbium and europium;

practically insoluble: cerium, lanthanum, neodymium, praseodymium, samarium and scandium.

The thorium double salt is also practically insoluble. As has been indicated, this differential solubility effect has been applied widely

throughout the years in gross rare earths separations, but as such is hardly to be construed as an analytical technique. A slightly different light is, however, shed by considering Marsh's modification⁽²⁰⁾. This worker found the sodium double sulphates throughout the lanthanon series to be almost completely precipitated from solutions saturated with sodium chloride. Yttrium double sulphates are also thus precipitated, but the writer has found that this is not the case for the scandium double salt^(6, 8) which remains as soluble in brine as in saturated sodium sulphate solution. Except for scandium, therefore, the precipitation of rare earth double sulphates from brine solutions may legitimately be considered as a group reaction for detection of the rare earths.

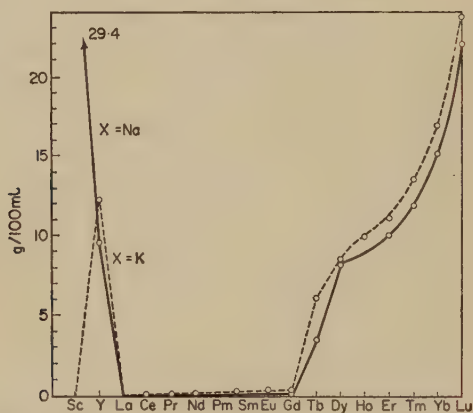


FIG. 3-2. Solubilities of $\text{RE}_2(\text{SO}_4)_3$ in water at 25°C .

Several variants of the oxalate, double sulphate, theme have been variously suggested in the literature as group tests, and it would seem significant that of qualitative chemical tests these two precipitation reactions in combination, present the only direct wet method capable of selectively detecting the presence of the rare earth group in an unknown material.

Beck⁽²¹⁾ has suggested the use of pyrocatechol for the selective precipitation of the rare earths, and to some extent this reagent can be considered of value in their detection and determination. The pyrocatechol complexes of the rare earths are said to be less soluble than are the oxalates. In ammoniacal systems, or those containing

ethylenediamine, almost all heavy metal complexes are soluble. Those of the rare earths are precipitated upon boiling. Beck has found that the sensitivities of the rare earth elements to this mode of precipitation are:

La:	100 μg ml
Y:	5 μg ml
Gd:	10 μg ml
Er:	100 μg ml

Beck has, moreover, also pointed out that the scandium and yttrium pyrocatechol complexes are soluble in sodium carbonate solution. Herein may well lie a method of further separation and detection and further work in this area would seem to be warranted.

Except possibly in the instance of cerium (*vide infra*), there is extant no direct colorimetric test for the detection of the rare earths as a group when in admixture with other elements. Somewhat paradoxically, a prior separation of the rare earths from associated elements has to be effected before one can even test chemically and colorimetrically for the presence of rare earths. Although many suggested procedures are found to be based somewhat upon empiricism, some application can be made in conservative systems such as might be obtained by a prior precipitation of the rare earth oxalates, or upon a solution believed to contain either the rare earths or other elements.

In conservative systems several qualitative tests have been applied. Wenger, Duckert and Rusconi⁽²³⁾ and Charlot⁽²³⁾ have critically examined many of the 'spot' tests suggested by other workers and found the *o*-toluidine or alizarin procedures to be the most reliable and sensitive. Of the two techniques, however, the author prefers the latter following the directions of Rinehart⁽²⁴⁾. At pH 4.5 the addition of 2 ml of 0.1 per cent Alizarin Red S solution to 3 to 5 ml rare earth solution will demonstrate the presence of as little as 8–10 γ rare earth with optimum sensitivity in the region 8–120 γ .

Many workers have suggested that, as a colorimetric test, there be used the colour reaction between iodine and basic acetates, benzoates, etc., of the rare earths. Kimura and Ikeda⁽²⁵⁾ and earlier, Kruger and Tschirch⁽²⁶⁾, examined these reactions and found that whilst yttrium, gadolinium and erbium acetates or benzoates develop no colour when treated with iodine, the lanthanum, praseodymium, neodymium and

samarium salts yield colours which darken to indigo blue on heating.

Several phenolics, hydroxyphenolics, quinolinols and alkaloids have been suggested at various times as reagents for the development of colour with the rare earths⁽²⁷⁾, but even in highly conservative systems and free from the multitude of interfering elements, sensitivities of the reactions suggested are usually very slight.

Beck has suggested⁽²⁸⁾ use of the potential bivalency of europium and ytterbium in systems for their detection. When reduced by zinc in acid solution europium gives a violet dye with cacotheline. Ytterbium, when reduced to the 2^+ state by sodium amalgam reacts with oxalic acid to form glyoxylic acid which in turn gives a red colour with naphthoresorcinol. Used in conservative systems, the foregoing reactions are specific for europium and ytterbium, but are not very sensitive.

Increasing interest has been paid to the problem of providing a 'spot' test for scandium and many suggestions have been made for the use of the alizarins⁽²⁹⁾. Beck⁽³⁰⁾ has shown the phosphate group to be almost specific for scandium and particularly in the form of inositol, phytin, etc., but the closest approach to a direct colorimetric test would appear to be that based upon 2,5 dihydroxy-1,4-benzoquinone which gives a pink precipitate with Sc concentrations of 3×10^{-4} M or better. In 3 ml of solution the minimum amount of scandium detectable is 0.04 mg⁽³¹⁾. Kuznetsov⁽³²⁾, however, recommends use of *o*-aminophenylarsonic acid which, when added together with salicylaldehyde to an acetic acid solution of scandium gives an intense yellow colour detectable at concentrations of $1:2 \times 10^6$. In conservative systems this is indeed an excellent method for the detection of scandium providing titanium and thorium are absent.

In the presence of other metals, probably the closest approach which the analyst can make to detection of rare earths by colorimetric spot tests is based upon the colour change of Ce^{3+} on oxidation to Ce^{4+} and the detection of the latter ions by virtue of their oxidizing power. Even in this the reactions and colour development involved are paralleled to some extent by those of e.g. manganese, chromium, iron, etc. Nevertheless, if such tests can be made upon conservative systems such as would be obtained by e.g. double sulphate, oxalate or in some instances hydroxide precipitation, then some indicative evidence can be obtained for the presence of cerium. If a neutral

solution be prepared from any of the conservative sources, cerium may be detected by

- (a) addition of the test solution to a large excess of saturated potassium carbonate solution containing hydrogen peroxide. Development of a yellow to orange colour is indicative of cerium. Conca and Merritt⁽³³⁾ claim to detect 0.056γ Ce/cm³ by this means.
- (b) addition to the test solution of an ammoniacal solution of silver nitrate will deposit a brown-black precipitate of silver if cerous salts be present.
- (c) treatment of the test solution with ammonium acetate solution and hydrogen peroxide will produce a yellow to orange colour or brownish precipitate if cerium is present in concentrations higher than 0.1 per cent.

Several reactions and colour developments have been suggested, however, which are claimed to have greater sensitivity than the foregoing. In general these reactions are based upon the oxidation of cerium to the 4⁺ state and use of this to oxidize brucine, leucomalachite, *p*-phenitidine, benzidine, etc., to intense dyes⁽³⁴⁾. In general such reactions are sensitive to 2γ Ce providing other, oxidizing, elements are absent.

Because qualitative wet chemical examination of an unknown will pass through the conventional analytical groupings, it is necessary to consider the general behaviour of the rare earths in these groupings. Rare earth chlorides being highly soluble we expect to find little if any, rare earths in chloride precipitates of silver, lead, mercury, etc.; occlusion, or co-precipitation, if it does occur, will be of infinitesimal quantity and as such can generally be disregarded. In the acid sulphide precipitate, mild occlusion will occur⁽³⁵⁾ but double precipitation will adequately remove all but negligible quantities of any rare earths. The ammonia precipitate of analytical group III elements will contain the rare earths but the completeness of precipitation will be a function of pH, NH₄⁺ ion concentration, anion species and the rare earth concentration as well as upon the specific rare earths present. The rare earth hydroxides require an excess of ammonia for precipitation and an excess of ammonium salts can be harmful. Fractional precipitation of rare earths by ammonia, as gas, or in solution in the

presence of ammonium chloride or nitrate is a simple means of concentrating lanthanum or yttrium in the mother liquor or filtrate⁽³⁶⁾ but their almost amphoteric nature renders ammonia precipitation of the hydroxide valueless from the analytical standpoint.

In hydroxide precipitation, as with the oxalates, carboxylate anions effectively inhibit or even prohibit precipitation. pH of precipitation and solubility products of the rare earth hydroxides were determined by Moeller and Kremers⁽³⁷⁾ but the data given by these workers and reproduced in Table 1 must be considered further from the aspect of ageing and hydrolysis of the precipitate just as in the case of scandium oxalate (above). Many solubility data have been obtained for many rare earth compounds but only infrequently do these data coincide with observations on limits of detection. Since 'ageing' and hence insolubilization is essentially a rate process we must expect to find gross differences in solubilities based upon limits of detection and those determined upon 'aged' precipitates of different hydration characteristics.

The ammonium sulphide group will in general occlude few of the rare earths which escape ammonia precipitation. We cannot expect hydrolysis at this point to be any greater than in the ammonia treatment, but occlusion in the ammonium sulphide precipitate tends to be a little higher than in the acid sulphide treatment. Here again, occlusion and co-precipitation can be reduced to a negligible degree by reprecipitation.

Precipitation of the rare earths together with the alkaline earths group will depend largely upon the precipitant employed for these fourth analytical group elements. If classical carbonate precipitation be employed, appreciable quantities of the rare earths will escape precipitation. Rare earth carbonates as conventionally prepared are invariably basic salts or double carbonates of appreciable solubility in excess of precipitant⁽⁸⁾. This solubility will persist even in the presence of appreciable quantities of, for example, calcium, which might otherwise act as a 'carrier'.

If, however, the alkaline earth group be precipitated as oxalates, entrainment of residual rare earths will be markedly improved; calcium oxalate is an excellent 'carrier' for the rare earths even in the presence of ammonium salts.

Except for scandium there is likely to be but little rare earth content in the final solution of the alkali metals. However, because of its

amphoteric nature and the ease with which it forms strong aquo-complexes, scandium is the most recalcitrant of the group, and some can be expected to pass into the alkali metal group, especially if present in only minor quantity. Lack of knowledge by the earlier scientists of the chemical behaviour of scandium renders almost a certainty the possibility that, in early analyses of, for example, euxenite, xenotime, davidite, etc., scandium may have escaped detection and been recorded with the alkalis when these were determined *in toto*, or missed completely when they were separately determined thus contributing to the summation error. Re-examination of many of the heavy lanthanon minerals for scandium would be an interesting exercise from which enlightening results might be expected.

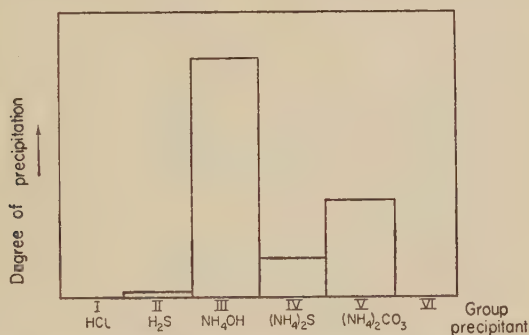


FIG. 3-3. Total rare earth precipitation levels with analytical grouping.

The general progress of the rare earths through the analytical series is shown diagrammatically in Fig. 3-3. Throughout any analytical sequence however it must be emphasized and continually borne in mind that precipitation of the rare earths by any reagent depends to a large extent upon associated ions – and particularly the anions. This is particularly so in the ammonia and oxalate (or carbonate) precipitations. If phosphate ion is present the rare earths will be quantitatively precipitated as phosphate upon the addition of ammonia. Even scandium is unlikely to miss precipitation thus – indeed phosphorus containing anions particularly hypophosphite, are probably the closest approaches to quantitative reagents for this element ^(8, 30, 38). In the presence of sulphate ion the hydroxide precipitate will be not pure hydroxide, but in part basic sulphate.

Similarly, when the hydroxides are precipitated from nitrate solutions the precipitate can be expected to be partially basic nitrate.

The main sources of rare earths being monazite, euxenite, xenotime, bastnaesite, uraninite, etc., rare earth products from the decomposition of these minerals may be expected to be associated with thorium, silicon, titanium, iron, aluminium, calcium, magnesium, uranium and possibly beryllium and copper. The extent to which these elements will contaminate fractions and accompany them in separations has been considered at some length in the writer's earlier work⁽⁶⁾ but it is appropriate here to consider more concisely the analytical implications of such geochemically associated elements and their analytical separation from the rare earths.

Classical chemistry indicates that we should expect elements associated with the rare earths to be separated from them by the following procedures:

oxalic acid in acid solution; elimination of Na, Al, Fe, Be, Ti, P, Ca, Mg, Mn, Co, U, Cu.

ammonia precipitation: Ca, Mg, Mn, Co, Na, Cu.

fluoride precipitation: Al, Be, Si, Ti, P, Na, U, Fe.

carbonate: P, Na, U, Al.

double sulphate: Al, Fe, Ti, U, Mg, Co, P, Cu.

phosphate: Mg, Mn, Co, Na, U.

Oxalate precipitation has been considered above. The essential factor in ammonia precipitation would appear to be the concentration of ammonium salts. High concentrations of these will effectively prevent gross precipitation of Ca, Cu, etc., but the concentrations of ammonium ions thus required would be equally as effective in inhibiting precipitation of lanthanum for example and would certainly prohibit precipitation of scandium.

Where fluoride precipitation is employed to remove uranium from the rare earths valence states must be considered. Uranous fluoride is insoluble and the sexivalent fluoride soluble. Silicon is possibly the only element which legitimately may be considered to be quantitatively removed in fluoride systems and this only when the precipitated fluorides are ignited with sulphuric acid. In the absence of sulphuric acid or perchloric acid some aluminium and titanium may be removed by hydrofluoric acid treatment but the separation cannot be expected to be complete.

Precipitation of the rare earths as carbonates is rarely carried out in analysis although some separations have been based thereon. If phosphorus is to be removed by this technique in monazite analysis for example, the optimum procedure would appear to involve direct decomposition of the ore by sodium carbonate fusion followed by aqueous leaching. Aluminium will then also appear in the solution together with a little lanthanum, yttrium, lutetium and any scandium which may be present.

None of the separation procedures listed above will effect absolute removal of thorium from the rare earths and, although it has been suggested that thiosulphate, peroxide or hexamine treatments are adequate for the separation, Moeller and his co-workers⁽³⁹⁾ concluded iodate precipitation to be the optimum procedure and in this the author concurs.

Despite the development of interest in 'spot' reactions the final method for detection of the rare earths devolves onto the spectro-scope or spectrophotometer. The only simple direct and unequivocal method for the detection of the coloured rare earths lies in observation of their absorption spectra by direct vision spectroscopy. In any laboratory, no matter how well instrumented it may be, if work is intended upon the rare earth elements, the possession of a small hand spectroscope for visual absorption studies is an essential item of equipment. Quantitative analysis by spectrophotometric techniques will be considered in a later chapter. Here we shall briefly consider the qualitative aspects observable by simple means. The visible absorption spectra of the rare earths are clearly discernible from Fig. 6-1. The praseodymium bands in the 590 $m\mu$ and 480 $m\mu$ regions, neodymium bands at 576 $m\mu$ and 522 $m\mu$ are all strongly evinced in solutions. Likewise the holmium spectrum at 537, 486 and 450 $m\mu$ and the absorption of erbium at 523 and 487 $m\mu$. All of these bands are intense and, when present together present distinctive and highly definitive evidence for the presence of rare earths. It is unlikely in normal procedures that the analyst will view the bands of a single element; the probable combinations are of course those of neodymium-praseodymium and holmium-erbium. With a good light source (100 watt lamp at 12 in) and an instrument of even moderate dispersion, rare earths are detectable by direct observation of their absorption spectra at concentrations down to about one part in ten thousand. Limits of detection are dependent of course upon the

particular rare earths present and the depth of solution examined. The neodymium–praseodymium groupings are visible at 1 : 20,000 concentrations through 2 in. depth of solution, those of the holmium–erbium complex at 1 : 2000 concentrations under the same conditions. At higher concentrations it is not even necessary to employ solutions for inspection; hydroxides, oxalates, carbonates and even oxides can be examined directly by reflected light and the band spectra easily observed without further treatment. Although some diffusivity may develop when iron, cobalt, manganese etc. are also present in solution, once the analyst has acquainted himself with these absorption bands they will be found peculiarly discernible under even the most obscure conditions. It must be remembered that observation of absorption bands merely indicates the presence of some specific rare earths — these may be any one or a mixture of the coloured earths. Visual absorption spectra will not show the presence or absence of lanthanum, cerium, europium, gadolinium, terbium, dysprosium, thulium, ytterbium, lutetium, yttrium or scandium. The possible presence of lanthanum and cerium can only be inferred by their customary co-occurrence with neodymium and praseodymium and of yttrium and dysprosium by their normal association with holmium and erbium.

Whilst considering direct spectroscopic methods of rare earth detection, we cannot omit those techniques which depend upon the development of coloured dyes by reaction with, for example, alizarin, morin, etc., but which, not being sufficiently specific for the rare earths depend upon selection of an absorption wavelength which may be different from that of the dye produced by otherwise interfering elements. In general, however, recourse to this technique requires spectrophotometric means in order that the wavelength of maximum absorption be adequately selected. In this context therefore, such methods of analysis will be considered in a later chapter.

Although not strictly methods for chemical detection of the rare earths we cannot close this chapter without reference to the use of fluorescence techniques for detection. Applied by several workers, this method of detection has not found much favour although the limits of detection are very small — 10^{-6} g/g. Because of the specificity of the techniques employed by Servigne and other workers reference to the original papers should be made by the analyst intending to apply this technique^(17, 40).

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CHAPTER IV

SEPARATIONAL PROCEDURES

ALTHOUGH IN many instances the instrumental analytical techniques considered in later chapters can be applied adequately to mixtures of all the rare earths, it is frequently necessary and preferable, in the interests of accuracy and to avoid interferences, to apply these techniques to conservative systems, i.e. those containing only one or two elements. The attainment of such conservancy, although generally a qualitative matter, can, with appropriate attention to details be made to approach quantitiveness. But the techniques which can thus be applied are few.

The ultimate desideratum, of course, would be separation of a system into as many individual components as possible, analysis of each fraction separately and summation of the results. Appreciable analytical errors may be expected to arise by use of such a procedure, however, and a happy medium must be sought which will provide for both accuracy and precision. By judicious handling, group precipitants such as oxalate⁽¹⁾ and carbonate⁽²⁾ can afford some degree of separation when applied through homogeneous precipitation procedures, but the overall precision is not good and results are rarely reproducible from analysis to analysis. Fractional precipitation of the mandelates⁽³⁾ has, however, been shewn to be of value and to be highly selective, with the elements appearing to precipitate in the reverse order of their relative basicities. Detailed description of the procedure involved would be valueless since the reported work selected reagent quantities, pH, and volumes to fit each experiment. Generally, however, the rare earth oxides are dissolved in hydrochloric acid, mandelic acid is added and the desired pH of precipitation obtained by the addition of ammonia solution.

Precipitation of the double alkali sulphates will, if properly handled, produce conservative systems of the light (La-Gd) and heavy (Tb-Lu) lanthanons with yttrium concentrating with the latter, and scandium precipitating with one or the other group, according to

temperature and the particular alkali sulphate employed for precipitation. As in all precipitation systems, however, solubility effects are pronounced and, whilst it is possible to ensure precipitation and separation of the light earths from the heavy, the converse does not hold.

Schoeller and Powell⁽⁴⁾ approve of double sulphate precipitation for coarse separation, but the technique they give is capable of some improvement, as follows.

Procedure: Adjust the rare earth solution, as chloride, nitrate, etc., to contain *ca.* 50 g oxide/litre and heat to 85°C. Sift solid, anhydrous sodium sulphate into the solution with constant stirring. The rate of salt addition should be such that the solution temperature is lowered by no more than 5°C. Add sodium sulphate until the Nd-Pr absorption spectra are no longer visible through a solution depth of 4 cm. Care should be taken at this point to differentiate between the absorption lines of Nd-Pr and erbium. At the point of disappearance of the Nd 576 m μ band, add solid sodium chloride to give a 1 per cent solution. Allow to cool and stand overnight. Filter off the precipitated double sulphates and convert by metathesis with caustic solution to hydroxides (*vide* Chapter II). Wash free of sulphate and excess alkali, redissolve in nitric acid for further examination. The original filtrate may be retained as such or the rare earths contained therein may be precipitated as hydroxides, oxalates, etc.

By this technique, the following separation can be achieved:

<i>precipitate</i>	<i>filtrate</i>
La,Ce,Pr,Nd,Sm	Gd,Tb,Dy,Ho,Er
Eu,Gd,Tb.	Tm,Yb,Lu,Y,Sc.

By replacing the sodium sulphate by the potassium salt any scandium present will be found with the light lanthanons in the original precipitate but will be lost on hydroxide metathesis.

In the analysis of yttrium, or heavy lanthanon, minerals where careful and adequate removal of the light lanthanons is necessary, effective use may be made of the sulphamate hydrolysis technique of double sulphate precipitation⁽⁵⁾. Rare earth sulphamate solution is treated with sodium nitrite to form and precipitate the double sulphates according to



Procedure: Dissolve 5 g of cerium-free rare earth oxides, or hydroxide equivalent, in slight excess of 50 per cent sulphamic acid solution. Filter

off insoluble material, silica, etc., and cool the solution in an ice bath. Add solid sodium nitrite slowly to the solution with constant stirring until the supernatant liquor shows removal of neodymium absorption spectrum. Filter off the precipitated sodium double sulphate and treat the precipitate and filtrate as above.

As an alternative to caustic metathesis, it has been suggested⁽⁶⁾ that the double sulphate be redissolved in ammonium acetate solution and reprecipitated as oxalate, but it is doubtful whether final precipitation under these conditions will be complete (*vide* Chapter III and reference 6).

An alternative route to precipitation of the double sulphates from homogeneous solution is *via* the use of the author's sulphite-sulphate oxidation technique⁽⁷⁾ in which a rare earth double sulphite solution is homogeneously oxidized to the double sulphates by passing air or oxygen through the hot solution.

Procedure: (a) Adjust the pH of 10 per cent rare earth chloride solution to 1.4. Add 5 g sodium sulphite ($\text{Na}_2\text{SO}_3 \cdot 7\text{H}_2\text{O}$) and heat to 80°C. Pass oxygen through the solution at a convenient rate (*ca.* 10 ml/sec) until precipitation has reached sufficient proportions. Filter off the double sulphate precipitate, add a further 5 g of sodium sulphite and repeat the operation, continuing until the desired extent of separation has been reached. Again, this can be adjudged by visual observation of the neodymium absorption spectrum.

(b) Slurry rare earth hydroxides, obtained by metathesis of oxalates, etc., or by ammonia precipitation, with sufficient water ultimately to yield a 10 per cent solution. Pass SO_2 through the slurry until solution is obtained. Add sodium sulphite to the solution as in (a) and oxidize by passing air or oxygen through the solution as above.

For an adequate separation of the light and heavy earths, double sulphate precipitation can also be made to take place homogeneously from chelated solutions of the rare earths with the sodium salt of ethylenediaminetetraacetic acid⁽⁸⁾. Again, rare earth hydroxides are obtained in solution with sodium 'enta' and the pH adjusted to 5.5–6.0 in the hot. The stirred solution at 50°C is then treated with sodium sulphate and heated cautiously. Precipitation usually occurs at about 60–80° with good grain size of the double salt and enhanced selectivity.

As will readily be appreciated, however, the foregoing procedures are essentially fractional in nature and require at least a modicum of experience to convert them to quantitative procedures. It must be

remembered moreover that, regardless of the technique of precipitation which may be employed, some co-precipitation of alien elements inevitably occurs (Chapter III, see also Vickery⁽¹⁾).

The most direct, and probably the most frequently employed, separation in analysis of the rare earths is that of cerium removal by oxidation hydrolysis procedures⁽⁹⁾. The ceric ion — Ce^{4+} — is relatively unstable above pH *ca.* 3.0. Cerium may therefore be selectively precipitated as hydroxide, etc., by oxidation in solutions of low acidity, providing that the point of precipitation of the other rare earth hydroxides or basic salts is not reached. Three techniques for this precipitation lend themselves to analytical application: these are based upon oxidation by iodate⁽¹⁰⁾, bromate⁽¹¹⁾ and permanganate⁽¹²⁾.

Because these procedures lead directly to the obtaining of cerium as oxide, oxalate, etc., they are admirably applied as gravimetric procedures and, as such, are considered in more detail in the following chapter. In the iodate procedure the cerium in nitrate solution is oxidized with bromate and the iodate precipitated by the addition of KIO_3 solution in 1 : 2 nitric acid. At varying acidities the other rare earths have been found to precipitate and the separation achieved by this technique is dependent therefore upon the precipitation of ceric iodate at acidity levels at which the iodates of the other rare earths are soluble.

Because thorium is also precipitated by iodate (*vide supra*) Shaver⁽¹³⁾ examined the coprecipitation of rare earths under appropriate conditions. Trivalent rare earths coprecipitate with thorium iodate by a type of isomorphous replacement within the thorium iodate lattice and a correlation can be found between ionic radii of the rare earths and the extent of coprecipitation. We should therefore expect to find a similar degree of coprecipitation of the other rare earths with cerium unless adequate care is taken in the operation.

In the iodate procedure cerium is precipitated as iodate after oxidation, in the two bromate and permanganate methods oxidation and hydrolysis occur simultaneously with precipitation of ceric hydroxide or a basic salt.

Cerium is precipitated in good purity by the basic nitrate/bromate technique in which the neutral rare earth nitrate solution is boiled with several grammes of marble chips and sodium bromate. The function of the marble is to remove acid as it is formed upon oxidation of the cerium nitrate thus ensuring that the precipitate is not

redissolved in the growing acid concentration. Boiling of the solution is continued for several hours — if not conducted under reflux conditions evaporation losses must be made up by the addition of hot water.

Since the filtrate will contain calcium derived from the marble chips, the combined other rare earths therein will require a double precipitation as oxalate to ensure that the final oxides are relatively free of calcium. Apart from the tediousness of this operation and the introduction of calcium into the solution, the nitrate/bromate method of cerium hydrolysis suffers also from incompleteness and the occlusion of other rare earth hydroxides or basic nitrates. The average recovery of cerium by this technique is about 97.6 per cent in 99.8 per cent purity⁽¹⁴⁾.

The Roberts permanganate oxidation process has nothing to offer over the iodate procedure but is somewhat speedier than the nitrate/bromate procedure albeit at the expense of introducing much manganese into the cerium fraction and a little into the residual rare earth solution. Since average recoveries of cerium are 97.5 per cent in 98.5 per cent purity this procedure can hardly claim to be of much analytical application.

Where prior removal of cerium from a system is necessary in analysis, the writer prefers to employ either iodate precipitation or solvent extraction. The former has been considered above, the latter procedure as now preferred follows the technique suggested by Wylie⁽¹⁵⁾ — oxidation of cerium to the 4⁺ state being followed by extraction of the ceric nitrate complex with ethyl ether. Recovery of cerium from the organic phase is readily effected by shaking with a saturated aqueous solution of oxalic acid. Extraction of ceric cerium has been examined by several workers employing, for example, tributyl phosphate, butyl acetate, thenoyltrifluoroacetone, etc.⁽¹⁶⁾ and it has generally been accepted that the butyl phosphate extraction is preferable. As Wylie points out, however, whereas ethyl ether extracts less than 0.3 per cent of La_2O_3 from a 5 N nitric acid solution of lanthanum nitrate containing 65 g La_2O_3 per litre, butyl phosphate extracts from nitrate solutions 4–7 per cent La_2O_3 and up to 15 per cent Pr_2O_3 . Ether is therefore to be preferred for the separation of ceric cerium from the other rare earths in spite of the greater stability claimed for the butyl phosphate systems. Other disadvantages of butyl phosphate are the necessity for reduction of cerium before back

extraction into water and the reported necessity for an additional treatment to overcome phosphate contamination of the products.

Procedure (Ethereal Extraction): 100 ml acid nitrate solution of the rare earths containing not more than 5 g CeO_2 are oxidized by the addition of 5 g KBrO_3 . After cooling, the acidity is adjusted to 6 N. Extract the solution in a separatory funnel with an equal volume of peroxide-free ether. Shake for approximately 3 min to attain equilibrium. Separate the layers, running the denser aqueous phase into another funnel. Adjust the acidity of the raffinate again to 6 N by the addition of a further 25 ml HNO_3 and again extract with a fresh quantity of ether. Again separate the phases and combine the ethereal extracts. Shake the combined extracts with 100 ml of 10 per cent oxalate solution and allow the phases to separate. Run the lower layer of oxalate suspension through a Whatman 40 filter paper and wash the collected oxalates with warm water before igniting to oxide.

With two extractions by this process better than 99 per cent of the total cerium will be recovered from the ethereal solution which also extracts 84 per cent of the total nitric acid in the solution. To ensure absence of peroxides from the ether used in the extractions it should be equilibrated from ferrous sulphate solution before use. Care should also be taken to avoid the incidence of ultra-violet radiation on the ethereal solution of ceric nitrate during extraction lest reduction and consequent incomplete extraction occur.

(Tributylphosphate Extraction): Shake the oxidized cerium solution obtained as above, with an equal volume of purified tributylphosphate and separate the phases. Then shake the TBP solution with an equal volume of water containing 3 per cent hydrogen peroxide or hydroxylamine. Separate and filter the aqueous phase through a Whatman 40 paper and precipitate the cerium from the filtrate with oxalic acid, or as hydroxide, and ignite to oxide.

In many instances, organic solvent extraction of complex compounds has been indicated as applicable to rare earth separations for analytical purposes. In general such extraction processes suffer from the same trouble as most other rare earth separation techniques — they are essentially fractional in nature, and require much experience in operation before anything approaching adequacy can be obtained.

There would appear to be few other techniques which are directly applicable to specific rare earth separations although Reddy⁽¹⁷⁾ has claimed the separation of lanthanum from all rare earths except cerium by precipitation as chromate from acetate solutions at pH 5.7.

In view of Hall's work on the chromate separation of rare earths⁽¹⁸⁾, however, applicability of the technique to analysis is dubious.

Fitch and Russell⁽¹⁹⁾ have satisfactorily applied selective ion exchange, to the separation of lanthanum from the other rare earths. In conjunction with other techniques of rare earth separation by ion exchange it would seem that the hydrazine-diacetic acid elution of rare earths might well be accepted as a technique for the specific determination of lanthanum; further work on this system is, however, required.

Several techniques, currently employed in separations of the rare earths, may in specific instances be applied to crude analyses. Examples of these are concentration of samarium, europium and ytterbium by Marsh's sodium amalgam process⁽²⁰⁾. Acetate solutions of the rare earths are shaken with 0.3 per cent sodium amalgam. Samarium, europium and ytterbium are thus reduced to the bivalent state and replace sodium in the amalgam taking with them very little of the other rare earths. Several repetitions of the process are, however, necessary on relatively concentrated solutions before extraction approaches completeness. The same situation applies also when the reduction-amalgam technique is effected electrolytically⁽²¹⁾. Several repetitions of these processes are necessary to give complete separations, and this only when the initial material has received some form of beneficiation. In view of the stringent requirements of these intricate procedures, reference is best made to the original papers.

It should be apparent at this point that the separation most applicable to rare earth analyses is that of cerium, and even here it is probably just as preferable to determine cerium by redoximetry on a separate sample. Where ion exchange analysis is, however, to be effected, prior removal of cerium is a requisite else cerium will almost invariably be found disseminated throughout the fractions.

Other procedures so far listed will of course yield separations of varying precision and, with the development of spectrophotometric techniques, the requirement has become even less necessary. Nevertheless, apart from the ease of working with conservative systems, quantitative analysis is improved and probably the simplest technique of separation of mixed rare earths into conservative systems is that of ion exchange. In an earlier, somewhat premature, volume⁽¹⁾ the author made the understandable mistake of relegating into the separational background all ion exchange procedures. At that time

this relegation was probably justified in view of the novelty of the technique and the author's conservatism. Now, however, it would appear quite legitimate to consider that ion exchange, supplemented by preliminary coarser techniques, and complemented by spectrophotometry and emission spectrography, represents the 'desideratum ultime' of rare earth analysis.

Perhaps the best system for rare earth separation by ion exchange thus far obtained is that employing EDTA elution through a resin column in the copper phase⁽²²⁾. For analytical procedures, however, adequate separations into conservative systems can be obtained by somewhat simpler techniques. For all normal purposes a column of Dowex 50 resin (200 mesh particles) 1.5×100 cm is satisfactory, particularly if it be surrounded by a heating jacket to maintain the temperature of the column at approximately 85°C . Samples of rare earth chlorides solutions up to 0.5 g oxide equivalent may be adsorbed onto such a column (with the resin in the hydrogen cycle) and eluted with 0.3 per cent citric acid of pH 5.0 at 75 ml per hour. The fractions obtained will then contain excellent concentrations of two or three elements at the most when the initial sample contained the whole gamut of rare earths. In this way many of the spectrophotometric interferences can be avoided and summations of analyses are unlikely to yield gross inaccuracies.

Before the work of Pollard *et al.*⁽²³⁾ several workers had suggested separation of the rare earths and associated elements by the use of paper or cellulose chromatography. Generally, however, the maximum separation had been that of thorium from scandium or from the rare earths⁽²⁴⁾. Pollard *et al.*, however, added oxine in butanol to the mobile phase and achieved separation of several rare earths upon both filter paper and cellulose columns. In both early and later work⁽²⁵⁾ small amounts only (*ca.* 1–200 mg) of rare earth oxides were crudely separated, use being made of the ultraviolet luminescence of rare earth oxine derivatives as a means of identification as well as spot tests developed for these specific systems. For qualitative analysis of a mixture the application of Pollard's technique would seem admissible, but it is doubtful whether it is readily applicable to gross analytical procedure without some refinement. Sato *et al.*⁽²⁶⁾ would seem to have initiated these attempts at refinement by the introduction of the electrochromatograph to rare earth analyses, but again only very small quantities were employed, electrolysis was conducted

over one or two days and the separation achieved could readily be duplicated on a much larger scale with more conventional procedures. Since this work, Lederer and his co-workers have further investigated this technique⁽²⁷⁾ and, with an acetylacetone mobile phase, effected good separations of e.g. neodymium and praseodymium. With an ammonium thiocyanate, ethanol/hydrochloric acid eluant, complete separation of the Nd, Sm, Eu group from gadolinium, etc. was readily obtained. Other workers have also contributed to this field⁽²⁸⁾ and, whilst it must be conceded that the limits of detection of individual rare earths by this technique are extremely precise (*ca.* 1×10^{-4} mol), much has yet to be developed to ensure adequate application of the principle to analytical technique. Possibly a column chromatograph with separation aided by the passage of an electric current will provide the ultimate answer to a rapid and accurate method of direct chemical analysis of the rare earth elements, or at least the more definitive production of conservative systems applicable to gross analysis. As an adjunct of paper chromatography it is interesting in this regard to consider the separation achieved by Duval and Kurbatov⁽²⁹⁾ of calcium from scandium by simple filtration of a chloride solution of the two elements through filter paper. Scandium was preferentially retained upon the filter paper by simple adsorption and separation was achieved from solutions containing about 10^{-4} M scandium and 10^{-3} M calcium.

Associated with the attainment of systems containing only a few rare earths, we have to consider the quantitative analytical separation of other elements from them. In the author's earlier work, ultimate purification of the lanthanons from alien elements was considered at some length. It will suffice here to review briefly the techniques applicable to specific elements, but it should not be forgotten that use of the mercury cathode will serve to eliminate all heavy metals from solutions of the rare earths, and, where possible, use should be made of this procedure. Aluminium is, in major proportion, removed by oxalate precipitation of the rare earths from acid solution. Approximately 2 per cent may contaminate an oxalate precipitate if large amounts of both aluminium and lanthanum be present. Double precipitation of the rare earth oxalates will, however, suffice to effect adequate and quantitative separation.

Small amounts of barium may be coprecipitated with rare earth oxalates and may be tenaciously held. If its presence is suspected it

may be removed by the addition of a small amount of sulphuric acid to the hot rare earth solution, followed by the stirring in of paper pulp and overnight standing. Any barium sulphate thus formed will be occluded in the pulp and may be readily filtered off without loss of rare earth material.

Beryllium is effectively removed by oxalate precipitation of the rare earths unless much aluminium is also present. Double precipitation of the rare earth oxalates will completely free them of both aluminium and beryllium at the same time.

The rare earths and calcium are almost symbiotic and some difficulty can be expected in obtaining the rare earths completely free of calcium. Alternate precipitation of the rare earths as hydroxide, oxalate, hydroxide, oxalate, etc., will ultimately remove all traces of calcium, the number of repeated operations necessary being dependent upon the initial ratio of rare earths to calcium and, in particular, the lanthanum content. Some rare earths can be expected to be lost during such repeated precipitation and redissolution and it is probably best, where many separations of the rare earths from calcium have to be undertaken, to institute an ion exchange procedure which, whilst eliminating all calcium from the rare earths will also effect a modicum of separation of the latter.

We have already considered some of the difficulties encountered in removing iron from rare earth systems by oxalate precipitation of the latter. When large amounts of rare earths are present with small traces of iron, separation is easily effected by oxalate precipitation. When iron and the rare earths are present in approximately equal proportion, recourse has to be made to double sulphate precipitation — but preferably only when the rare earths present are those of the light lanthanon group. When iron predominates and/or the heavier earths are present in major proportion, some difficulty can be expected. Fluoride precipitation may be undertaken with some care, but even this is to be avoided when high iron contents are associated with small amounts of the rare earths. In such systems the $[\text{FeF}_3]$ complex dissolves rare earth fluorides with some avidity forming double complexes of some stability. Unpublished work has shown that the solubility of rare earth fluorides in an iron fluoride complex solution increases from lanthanum (0.5 g/l.) to lutetium (1.3 g/l.) with YF_3 dissolving to the extent of 1 g/l. The solubility of scandium fluoride was not determined, nor was the effect of pH, salt concen-

tration, etc. However, the results obtained indicated clearly that care must be taken before deciding to remove large amounts of iron from small amounts of rare earths by fluoride precipitation. Regardless of the tediousness of operation, it can be considered that under the circumstances indicated, the preferable methods for such a separation are either the Rothe ether extraction of iron or ion exchange processes. The mercury cathode may be used when the sample is small; the rare earths are then precipitated from the electrolyte with oxalic acid, or the residual iron removed with ether. Too much emphasis cannot, however, be placed upon the care with which the analyst must conduct separation of iron from the rare earths.

Removal of appreciable amounts of magnesium may present problems; even after two precipitations of the oxalates from acid solutions as much as 0.5 per cent MgO may still contaminate the precipitate. If, however, the two oxalate precipitations are alternated by an hydroxide precipitation in the presence of ammonium salts, the final oxide should be completely free of magnesium, albeit minor amounts of lanthanum and yttrium and much scandium may be lost.

Manganese may be removed by simple oxidation of the sulphate solution with ammonium persulphate. After filtering off the precipitated manganese oxide the rare earths are recoverable from the filtrate completely free from manganese.

Phosphates will rarely be introduced into analysis of the rare earths except when pyrophosphate has been employed for the removal of thorium or in the precipitation of scandium. However, much phosphate can be expected to be present when the mineral origin of the rare earths is monazite, xenotime, etc. Co-precipitation of phosphate with rare earth oxalates, hydroxides, carbonates, etc., is well known and even double sulphate precipitation will leave as much as 1 per cent P_2O_5 in the rare earths. There are few if any short cuts to the complete removal of phosphorus. Two sodium peroxide or hydroxide precipitations interspersed with two oxalate treatments are necessary for ultimate purification of the rare earths from phosphorus.

Removal of alkalis from a precipitate is an omnipresent problem in any phase of gravimetric analysis. It is not lessened in rare earth analyses. Apart from their individual presence, much of the difficulty in dealing with the alkalis lies in the anion associated with them. It is

this, for example, which renders the removal of sulphate from rare earth systems such a tedious procedure. Sodium is more strongly occluded in oxalate precipitates than is potassium and basically the only means for ultimate removal of the alkalis is continued precipitation of the hydroxides with ammonia.

Although their presence will only become a major problem in analyses of samarskite, fergusonite, etc., the earth acids, tantalum and niobium, should always be expected in a mixed mineral examination. After decomposition of the ore, removal of these two elements is readily accomplished by exhaustive hydrolysis by boiling the rare earths solution at pH *ca.* 5.0. Prior reduction of cerium to the trivalent state is necessary else hydrolytic precipitation of this element will also occur. The addition of a little paper pulp to the boiling solution will aid collection of the finely divided hydrated tantalum and niobium oxides. The tantalum and niobium precipitate should be redissolved in concentrated hydrochloric acid and rehydrolysed, the second filtrate being added to the first for adequate recovery of the rare earths. Not only must tantalum be expected in ore samples; in the calcothermic preparation of the rare earth metals, the use of a tantalum crucible liner tends to deposit some of this metal at least in the surface of the metal ingot. In metal analyses tantalum should also therefore be the object of examination.

Moeller *et al.*⁽³⁰⁾ have reviewed several methods for the separation of thorium from the rare earths. The procedure which has now been found to be most effective is precipitation of thorium iodate from a reduced nitric acid solution. If the solution contains an oxidant then cerium also will be precipitated with the thorium. Hydrogen peroxide should not at this stage be added as a reducing agent; one or two ml of saturated oxalic acid solution will effect this reduction and yet be insufficient to precipitate the rare earths at the acidity of thorium precipitation. Removal of thorium with potassium iodate is complete in one operation but the precipitate should be redissolved and reworked for the ultimate removal of rare earths occluded in the first precipitate. Stine and Gordon⁽³¹⁾ determined the degree of separation of thorium from the rare earths and Shaver (*loc. cit.*) has, conversely, determined the coprecipitation of rare earth iodates with thorium iodate when precipitated from homogeneous solution. About 0.4–0.5 per cent rare earths can be expected to precipitate together with the thorium iodate.

Removal of thorium from the rare earths by precipitation with thiosulphate⁽³²⁾ or hexamethylenetetramine⁽³³⁾ is not to be recommended. The first process also precipitates scandium whilst the second strongly coprecipitates and occludes the heavier lanthanons. Moeller and Schweitzer⁽³⁴⁾ have suggested the use of pyrophosphate as a reagent for this separation, but too little is known about its applicability to warrant general usage. Certainly any precipitation with pyrophosphate will carry down scandium. It is felt that the only alternative to iodate treatment is precipitation of thorium from a neutral nitrate solution with hydrogen peroxide⁽³⁵⁾. The nitrate solution is evaporated to dryness for removal of free acid and redissolved in 100 ml of 10 per cent ammonium nitrate solution. Precipitation is then effected by the addition of 25 ml of 10 per cent hydrogen peroxide to the warm solution. The precipitate again has to be reworked for reclamation of occluded rare earths. Precipitation of thorium by oxine from EDTA complexed solutions has also been recommended⁽³⁶⁾.

Titanium will normally be hydrolysed and precipitated together with the acid earths (*vide supra*). If, however, hydrogen peroxide is present, e.g. from initial attack of a mineral sample or reduction of cerium, the formation of pertitanate ions will cause much titanium to miss hydrolysis and remain unprecipitated. Oxalate precipitation of the rare earths is usually inadequate for removal of titanium from the system but double sulphate precipitation in the presence of hydrogen peroxide and brine will reduce the titanium content of the rare earth oxides to less than 0.001 per cent. Probably the best procedure, however, is to remove any peroxide present by boiling with a little permanganate and then to carry out hydrolytic removal of the titanium. Again the addition of a little paper pulp is helpful in entraining small amounts of hydrated titanium oxide.

Uranium is now known to contaminate both oxalate and double sulphate precipitates of the rare earths⁽³⁷⁾. Its precipitation by ammonium carbonate is rarely clean enough for analytical purposes, rare earth double carbonates frequently accompanying the uranium in the precipitate. Extraction of uranium nitrate by ether or hexanone⁽³⁸⁾ is, however, quite applicable. It is first necessary to ensure complete reduction of any cerium present to the tervalent state — again using oxalic acid — to prevent this element accompanying uranium into the organic phase. Two or three simple extractions of

the nitric acid solution are usually perfectly adequate for the analytical removal of uranium from the rare earth solution.

Zirconium, where not hydrolysed at an early stage, together with the acid earths and titanium, will tend to remain in solution when the rare earths are precipitated as oxalates. A few milligrammes may accompany the rare earths if the original concentration of zirconium was high. These are best removed by precipitation as the basic selenite with selenious acid⁽³⁹⁾. This separation is very clean and no occlusion of rare earths occurs when only small amounts of zirconium are to be removed from the system.

We have referred briefly above to use of the mercury cathode for removal of heavy elements from rare earth solutions, and have subsequently considered solely chemical techniques for this separation. For the most part the rare earths are not deposited in the mercury cathode from sulphuric or perchloric acid solution, the exceptions apparently being lanthanum and neodymium, for which Lundell and Hoffman⁽⁴⁰⁾ reported partial deposition. Marsh (*loc. cit.*) found some amalgam formation with these elements when using sodium amalgam in the reduction of samarium, etc., but the operation of the mercury cathode separation is such that we should expect, by potential control, to effect excellent separation of the rare earths, be they present singly or as a group, from the heavy metals. As Lundell and Hoffman (*loc. cit.*) and Maxwell and Graham⁽⁴¹⁾ have indicated, complete extraction into mercury can be expected for iron, cobalt, nickel, copper, zinc, gallium, germanium, rhodium, platinum, palladium, silver, cadmium, indium, tin, iridium, gold, mercury and thallium. Bismuth, chromium, molybdenum, rhenium and technetium are also thus extracted and some removal of arsenic, selenium, manganese, antimony and lead can be found.

It has been claimed⁽⁴²⁾ that use of the double cup electrolysis apparatus has given some separation of the rare earths from the alkali and alkaline earth metals, but the writer has been unable to confirm this.

For the major separations indicated, the procedure which has been found most applicable uses a 1 M solution of the rare earths in 1 M perchloric acid, or less preferably 1.5 M sulphuric, with 1 kg mercury in a cell giving a cathode surface of 350 cm². The mercury should be stirred by a magnetic stirrer and the apparatus is enclosed in a water jacket enabling temperatures of 50–60°C to be obtained. The solution

of rare earths, containing up to several hundred milligrammes of heavy metals is then electrolysed at about 6 V potential across the cell and a current density of *ca.* 0.25 amp/cm². Removal of all heavy metal contaminants is, in general, complete in about one and a half hours. The supernatant solution is then removed and the rare earths then further treated as necessary.

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CHAPTER V

NON-INSTRUMENTAL TECHNIQUES

QUANTITATIVE ANALYSIS of the rare earths is now almost entirely instrumental in nature, and indeed it is only by this development of instrumentation that quantitative analysis can be carried out effectively. Because applicable chemical dissimilarities through the rare earth series are almost entirely restricted to valence state variations⁽¹⁾ it is inevitable that we are constrained to consider only cerium, praseodymium and terbium, samarium, europium and ytterbium, as subjects for quantitative chemical analysis. Even of these elements only cerium and europium lend themselves to direct volumetric determination. Some aspects of the gravimetric determination of cerium have already been considered and will be given expanded treatment below. Praseodymium and terbium may be estimated (not determined) to moderate accuracy by analysis of the 'active oxygen' content of mixed oxides, but since praseodymium is more readily determined spectrophotometrically, the application of this technique is restricted somewhat to estimates of terbium, and oxide valency corrections of analysis summations.

Extraction of samarium, europium and ytterbium into sodium amalgam might be considered the basis of an analytical technique⁽²⁾, but it is applicable only to relatively concentrated systems and its analytical accuracy is of some doubt. Samarium is again more readily and accurately determined by spectrophotometry. Europium is just as readily determined by zinc reduction/permanganate oxidation⁽³⁾ or, together with ytterbium by polarography⁽⁴⁾. Chemical determination of individual rare earths in mixtures may therefore be considered almost solely applicable to cerium and possibly europium.

In specific instances, however, some other direct chemical evaluations are possible and permissible — precipitation titrations with ferricyanide, 'average atomic weight' determinations, etc. These will be considered later in this chapter.

Basicity hydrolysis procedures for the separation and purification

of cerium from other rare earths have been discussed in the previous chapter. With much attention to detail these — particularly the nitrate/bromate process — may be employed as gravimetric procedures. However, where cerium is to be determined gravimetrically, precipitation of the iodate is preferable, followed by metathesis or precipitation with oxalic acid and ignition of the oxalate to oxide.

IODATE PROCEDURES

Procedure: To a nitrate solution containing 0.1 g cerium in 50 ml add 25 ml of concentrated nitric acid and 0.5 g potassium bromate. Warm to dissolve the solid salt. Precipitate the cerium as ceric iodate by the addition of 50 ml of 0.1 per cent solution of potassium iodate in 1:2 nitric acid. Allow the precipitate to settle and filter through the equivalent of a Whatman 42 filter paper. Wash the precipitate twice on the paper with a solution of 1 per cent KIO_3 in 5 per cent HNO_3 , return it to the original beaker and digest for a few minutes with the same solution. Filter again and return the filtrate to the same beaker. Redissolve the precipitate with hot concentrated nitric acid and, after the solution is complete, cool somewhat and add a further 0.25 g KBrO_3 . Reprecipitate the cerium with another 50 ml of potassium iodate solution. Allow the reprecipitated iodate to settle, filter and wash as before, then transfer the precipitate to the original beaker. Add 50 ml of water and 10 g of solid oxalic acid and boil until cessation of iodine evolution. Allow the precipitated oxalates to settle overnight, filter, wash with warm water and ignite at 900°C to CeO_2 . Treat the filtrates and washings by oxalate or hydroxide precipitation for recovery of rare earths.

Aleksandrov and Tikhonova⁽⁵⁾ have suggested replacement of potassium iodate by the per-salt which in itself first oxidizes the cerium ion and then precipitates the iodate.

Procedure: Neutralize 100 ml of cerous nitrate solution (containing <0.1 g CeO_2) to methyl orange with NaOH . Add 3–5 g NH_4NO_3 and boil. Add 100 ml saturated aqueous solution of potassium periodate and continue boiling for 10–15 min. Add concentrated nitric acid to bring the acidity to 0.1 N and boil briefly. Filter off the precipitated ceric iodate and wash with 5 per cent NH_4NO_3 . Redissolve the precipitate in HNO_3 and H_2O_2 and repeat the precipitation. Treat the final iodate precipitate as above.

In that this procedure does not seem to require additional oxidizing agent it might appear preferable over the iodate/bromate technique. Other rare earths up to 750 times the weight of cerium are claimed not to interfere, but coprecipitation of thorium iodate can be expected if that element be present.

BROMATE PROCEDURES

Procedure: The nitrate solution should be nearly neutral and contain not more than 0.1 g of cerium in 200 ml. Add 5 g of potassium bromate and boil to the evolution of bromine vapour. Add several small pieces of clean marble chips and continue boiling. Carry out the operation under reflux conditions because boiling proceeds for several hours. Add further 0.5 g portions of KBrO_3 every 90 min. When a test drop of the supernatant liquid gives a negative reaction to hydrogen peroxide and ammonia (Chapter III), precipitation can be considered complete. Filter the basic precipitate on a Whatman 542 paper, remove the remaining marble chips with forceps, wash with 2 per cent sodium nitrate solution and return the precipitate to the original beaker. Redissolve in concentrated nitric acid with the addition of a few drops of hydrogen peroxide and evaporate to dryness. Take up with water and repeat the oxidation and precipitation. Treat the combined filtrates and washings further with bromate and marble to ensure precipitation of the last remnants of cerium. The finally collected precipitate is ultimately redissolved in nitric acid and reprecipitated as oxalate or hydroxide, then ignited to oxide at 900°C and weighed as CeO_2 .*

A combined volumetric-gravimetric approach is sometimes useful:

Procedure: The nearly neutral nitrate or chloride solution should contain approximately 0.1 g Ce^{3+} in 200 ml. Heat to 80°C and titrate with standard KMnO_4 - Na_2CO_3 solution to a permanganate pink endpoint.

Notes

1. The standard permanganate solution is preferably 0.1N in which 4 moles sodium carbonate have been added for each mole of permanganate. $1 \text{ ml } 0.1\text{N } \text{KMnO}_4 = 0.17212 \text{ g } \text{CeO}_2$.

2. In the primary reaction:



the liberated acid is neutralized by the co-added alkali. The endpoint is reached, of course, when the supernatant liquor above the precipitated hydrated cerium and manganese oxides shows the permanganate colour. Care must be taken to differentiate between the permanganate pink endpoint and the pale rose colour which also may develop due to neodymium ions and which appears when this element is present in reasonable quantity.

3. Because of the precipitated manganese oxide it is not permissible to over-titrate the permanganate and then back titrate with e.g. arsenite or ferrous ions. Check analysis may, however, be effected by filtering off the precipitate and converting the cerium hydroxide to oxalate by metathesis with 10 per cent oxalic acid, filtering this off and igniting to the oxide. This gravimetric check is, however, likely to be high owing to the occlusion of manganese and possible co-precipitation of other rare earths.

* A disturbing feature of this procedure is that some basic cerium salt adheres strongly to the marble surfaces. Care must be taken to ensure its recovery by a rapid attack by concentrated nitric acid.

PERSULPHATE OXIDATION

Auti⁽⁶⁾ and Weiss and Sieger⁽⁷⁾ made critical studies of the volumetric determination of cerium and recommended the original von Knorre method⁽⁸⁾ of persulphate oxidation of Ce^{3+} ions to the Ce^{4+} state followed by reduction with hydrogen peroxide, the excess of this reductant being determined with permanganate. Use of peroxide is, however, generally to be avoided and the most satisfactory results are to be obtained by the Willard and Young method⁽⁹⁾ which follows the persulphate oxidation by direct titration of the Ce^{4+} ions with Fe^{2+} solution using *o*-phenanthroline as indicator. Charlot⁽¹⁰⁾, however recommended *N*-phenylanthranilic acid as the indicator, but in practice any redox indicator may be employed whose colour change takes place at close approximation to the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox potential.

Procedure: Weigh 1 g of rare earth oxide mixture into a 500 ml Erlenmeyer flask, add 15 ml of concentrated sulphuric acid and heat to vigorous boiling until the sample has completely decomposed. Cool in ice and add 150 ml of cold water. If a clear solution be not obtained, the insoluble material should be filtered off and retreated and the solutions combined. Add 5 ml of 0.25 per cent AgNO_3 solution and 5 g of solid ammonium persulphate. Boil until excess persulphate is decomposed (15–20 min). Cool the solution and titrate with an excess of ferrous ammonium sulphate solution, determining the excess of ferrous solution by back-titration with permanganate or dichromate. The permanganate-ferrous solutions should have been previously standardized against each other and arsenite in the usual way

*Notes*

1. Emi⁽¹¹⁾ has suggested simple titration of the Ce^{4+} solution with titanous sulphate using diphenylamine sulphonate indicator; this would seem a convenient procedure although the stability of the titanium solution leaves much to be desired.

2. A disturbing feature of persulphate oxidation lies in the occasional reduction of Ce^{4+} ions when the solution is boiled. The orange colour first produced after the addition of silver nitrate and persulphate, sometimes suddenly disappears. From the kinetic studies of Fronaeus and Ostman⁽¹²⁾ this auto-reduction would appear to be attributable to several factors—presence of chlorides, too high acidity, or excess persulphate. The latter is the usual culprit since it leads to the subsequent formation of peroxide ions which reduce the ceric ions. In instances of autoreduction, addition of e.g. ferrous sulphate or a little oxalic acid followed by boiling to remove the excess persulphate should be followed by the addition of further silver nitrate and less persulphate. Boiling for a further 5 min then ensures complete oxidation.

SODIUM BISMUTHATE OXIDATION

Oxidation of cerium may also be effected by sodium bismuthate⁽¹³⁾ in a manner analogous to that employed in the determination of manganese.

Procedure: Dissolve the rare earth oxides in sulphuric acid as described above in the persulphate oxidation method. After cooling, add 10 ml of sulphuric acid and 100 ml of cold water. Add 1.5 g of sodium bismuthate and heat to boiling. Shake gently during oxidation to avoid adherence of bismuthate to the bottom of the flask. Boil for 1 min only. Dilute with 50 ml of 2 per cent sulphuric acid and filter through an ignited asbestos pad or a sintered glass filter which has been previously washed with concentrated nitric acid. After filtration to remove the excess of bismuthate, wash the filter with 100 ml of 2 per cent sulphuric acid. Cool the filtrate and washings and titrate with ferrous ammonium sulphate and permanganate as described above.

$$1 \text{ ml } 0.05 \text{ N KMnO}_4 = 0.008606 \text{ g CeO}_2$$

Direct titration of ceric ions with ferrous sulphate against, for example, diphenylamine is not to be recommended.

Such redox titrations may also be followed electrometrically using a platinum-silver chloride electrode system. The equivalence point is reached at 200–250 mV. Although most redox titrations for cerium require prior oxidation of Ce^{3+} ions, Goffart⁽¹⁴⁾ has been able to titrate the tervalent ion directly against permanganate using the amperometric end point.

It would seem clear from the published polemics that titration of cerium by ferro- or ferri-cyanide⁽¹⁵⁾ cannot be recommended. On the other hand, Joshi⁽¹⁶⁾ has demonstrated useful results from the titration of Ce^{4+} ions by thiocyanate. As a reducing agent the thiocyanate molecule corresponds to six equivalents, and the excess can be titrated in 2 N HCl by oxidation with potassium bromate, iodate or permanganate. More directly, the initial titration can be followed potentiometrically to a sharp end point. Where this latter is not desired or possible, iodine monochloride in carbon tetrachloride can be used as the indicator and titration carried to disappearance of the iodine colour.

Europium and ytterbium may be determined volumetrically after reduction to the 2^+ state. The titration of europium as first recommended by McCoy, and recently elaborated by Kremers (*loc. cit.*) is, however, applicable only to materials containing relatively high percentages of europium, or those in which it is associated only with,

for example, gadolinium or neodymium. Samarium has not been found to interfere, however, since its redox potential is too high to permit reduction by amalgamated zinc.

The original McCoy titration depended upon reduction of EuCl_3 to the bivalent state by zinc and its reoxidation by iodine.

Procedure: Obtain the chloride solution free from oxidizing agents, sulphates and phosphates. Dilute to 0.1–0.2 N acidity. Pass the solution slowly through a Jones reduction column containing 20–30 mesh amalgamated zinc and catch the reduced solution in an excess of 0.04 N iodine solution. The zinc column must never be allowed to dry at any part of the reduction and, as the rare earth solution percolates downwards, the column is progressively washed with 0.1 N HCl. The iodine solution after receipt of the reduced solution and washings is then titrated against standard thiosulphate solution.

1 ml 0.04 N iodine = 0.00704 g Eu_2O_3 .

Notes

1. The original rare earth oxides subjected to this procedure should contain not less than about 7 per cent europium, and ytterbium should be absent. The latter criterion is generally met by the geochemical association of the rare earths; the former can be met by shaking a solution of the earth acetates with 1 per cent sodium amalgam; samarium and europium then pass into the mercury phase. After separation of the two phases, the amalgam is back-extracted with 10 per cent HCl. Europium and samarium thereby concentrate as chlorides and the former may be determined volumetrically as above. For specific details of the amalgam extraction procedure, reference should be made to the original papers of Marsh⁽¹⁷⁾.

2. Since ytterbium chloride is also reduced in the Jones reductor, it may be determined, in the same way as europium, in chloride solutions of the heavy lanthanons. In such cases it is rarely necessary to concentrate ytterbium before determination, but when such a requirement does occur, recourse may again be made to the Marsh amalgam technique.

3. Ambrozhii and Luchinkova⁽¹⁸⁾ have suggested a semiquantitative method for the determination of ytterbium which is also obviously applicable to europium and samarium, and which would appear capable of yielding quantitative results if handled correctly. The basic procedure involves reduction of ytterbium (or samarium or europium) by sodium amalgam and then adding potassium iodate. Reoxidation of the bivalent ion thus liberates iodine which may be extracted into chloroform and titrated, or the excess of a known amount of iodate titrated by customary procedures. Insufficient data are, however, available fully to assess the value of the technique, which would seem worthy of further investigation.

The studies of Beck⁽¹⁹⁾ and Marsh⁽²⁰⁾ on the oxidation of praseodymium and terbium oxides to the higher valence state in fused hydroxide systems, have been applied to analytical procedures by Misumi⁽²¹⁾. Although the accuracy of the procedure is probably not

high, and praseodymium can adequately be determined spectrophotometrically, the technique may be of some interest where instrumentation is not available and estimations only are required.

Procedure: Precipitate the praseodymium (or terbium) containing hydroxides from solution with KOH. Filter and dry the hydroxides then fuse with KOH-KClO₃ in a nickel crucible (see Beck and Marsh, *loc. cit.*). Cool and leach the fused cake with water. Digest the extracted mass gently with 0.1 per cent acetic acid to dissolve residual neodymium, lanthanum, etc., hydroxides. Filter and attack the undissolved material with 7.5 N ammonia to dissolve any nickel contained in the oxide. The final residue is PrO₂ and may be weighed as such although final traces of neodymium still remain.

In terbium analyses, oxidation to the quadrivalent form can best be effected by electrolysis of the melt (Marsh, *loc. cit.*), but the extractive procedure can still be applied to the fused hydroxide cake.

Ambrozhi and Gol'tsev⁽²²⁾ have proposed a novel volumetric method for the determination of praseodymium based, apparently, upon its 'active oxygen' content. Both qualitative and quantitative procedures have been suggested, accurate, it is claimed, to 10 γ in a 1:1 $\times 10^6$ dilution.

Procedure: Remove cerium from the solution leaving no more than 1 per cent CeO₂. Evaporate the solution to dryness and ignite at 700°C for 2 hr. Weigh an amount of oxide, containing *ca.* 20 mg praseodymium, into a 100 ml Erlenmeyer flask. Add 4 ml of (5 per cent) MnSO₄ solution, and 12 ml of 1:3 H₂SO₄. Warm gently to the development of the permanganate colour. Cool and titrate with oxalate or arsenite in the usual way.

$$1 \text{ ml N/100 oxalic acid} = 0.002345 \text{ g Pr.}$$

Notes

1. By suitable adjustment of quantities of reagent, this procedure is directly applicable to qualitative examinations. In the co-presence of terbium some interference can be expected, but in separate systems it would seem that this technique could also adequately be applied to the volumetric determination of terbium.

2. The prime requirement is, of course, complete conversion of 3+ oxide to the 4+ state on ignition. Where this is not effected, accuracy of the procedure will fail.

Many methods have been claimed to be specific for various rare earth elements, but in general it is found upon subsequent evaluation, that they are specific for individual rare earths only when no other

rare earth is present in solution or, that specificity is dependent upon, for example, pH control, and that operations thus become little more than fractional separational procedures. Systems of this type are the oxinates, cupferrates, tartrates, etc. Recently, Bomberger⁽²³⁾ has suggested that hypophosphorus acid be considered a gravimetric reagent for scandium. Lanthanum and cerium were not found to precipitate with scandium, but yttrium did precipitate. No indications were given of behaviour of the other rare earths and correlation is thus difficult. It is also difficult to reconcile these results with the known similarities of reaction between scandium and the other rare earths, and it would seem that any specificity for scandium is related to basicity characteristics and thus elements such as lutetium, ytterbium, etc., would vitiate any results obtained from mixed solutions.

Before, and after, application of the spectroscope to rare earth detection and determination, early workers made much of 'average atomic weight' determinations in following the progress of their fractionation techniques and the purity of their products. With increasing use of the spectroscope this purely chemical analytical procedure has become almost an academic exercise and this is to be deplored; in competent hands excellent analysis can be obtained of bi-component systems, and of the state of purity of non-coloured rare earths when they are in process of purification. Accuracy is, of course, highest in such systems as La-Pr, Nd-Sm, Y-Er, Y-Ho, Y-Dy, or Sc-Yb and rapid analysis of such binaries can be made with an accuracy of ± 0.1 – 0.15 per cent.

Several methods have been suggested for average atomic weight determinations, the most common involving ignition of oxalate or sulphate to oxide. These ignition methods are, however, somewhat liable to error unless so carefully carried out as to render the procedure completely unsuitable for routine purposes. More accurate and preferable is determination of atomic weight via the oxide : oxalate ratio.

Procedure: Dissolve 0.5 g of oxides in 50 ml of 1 N H_2SO_4 in a covered 250 ml beaker. Heat gently to obtain solution. After dissolution add 50 ml of saturated potassium oxalate solution to precipitate the rare earth oxalates. Filter the solution into a volumetric flask and wash the precipitate with warm water. Dilute to the mark and withdraw aliquots for titration of excess sulphuric acid with standard sodium hydroxide using bromcresol blue indicator. If w_1 be the initial weight of the oxide, w_2

the weight of sulphuric acid combining with the oxide, then E_1 , the mean equivalent weight, is obtained from

$$w_1 : w_2 :: 2E + 48 : 3 \times 98 \quad \text{whence} \quad E = \frac{(294(w_1/w_2)) - 48}{2}$$

Note

There are many variations on this theme: dissolution of oxide in acid, neutralization, precipitation with excess oxalate and permanganate titration of the excess precipitant; dissolution of a known weight of oxalate in dilute sulphuric acid and titration of the liberated oxalate ion by permanganate. With the strongly basic oxides a known weight of oxide can be dissolved in excess of N/2 sulphuric acid and the excess of acid determined by direct titration against standard alkali with methyl orange as indicator.

Except in the estimation of Pr and Tb by fusion oxidation (above) it has been tacitly assumed, in all methods considered in this section, that the oxide used in the determinations has a composition represented by the generic formula RE_2O_3 . It is clear, however, that this cannot be the case if cerium, praseodymium, thorium or terbium are present in any appreciable quantity. In such instances those methods involving weighed quantities of oxides are valueless unless an appreciation of their higher oxide content be included in the calculations. Resolution of this situation is achieved by determination of the 'active oxygen' content of these oxide mixtures, i.e. the oxygen present in excess of that required for stoichiometric sesquioxide formation. Bunsen early made such determination by attacking the oxides with hydrochloric acid, absorbing the liberated chlorine in potassium iodide solution and titrating the liberated iodine⁽²⁴⁾. The insolubility of CeO_2 in HCl militates, however, against use of this technique with oxides whose cerium contents are higher than 40 per cent. Barthauer and Pearce⁽²⁵⁾ overcame this difficulty by using potassium iodide in the solvent.

Procedure: Attach a 500 ml Kjeldahl flask to a water-cooled reflux condenser, the upper end of which is attached to a tube bent in a semi-circle and terminating in a Bunsen valve. When in use, immerse the valve in potassium iodide solution contained in a small beaker. Weigh 0.2 g of oxide into the Kjeldahl flask and add 20 ml of 10 per cent KI solution. Place 80 ml of 4 per cent KI in the beaker enclosing the Bunsen valve. Add 10 ml of 12 N HCl to the flask, rapidly attach the reflux condenser and heat gently until dissolution of the oxide is complete. Cool and remove the vapour trap and wash any sublimed iodine into the flask. Dilute the solution to 350 ml and titrate to a starch end point with standard, 0.1 N,

thiosulphate. Determine a blank under identical conditions and make appropriate corrections — this should in no circumstances exceed 0.5 ml.

$$\text{mg Active oxygen} = (\text{ml Na}_2\text{S}_2\text{O}_3) (\text{N Na}_2\text{S}_2\text{O}_3) (\text{meq. O}_2)$$

The foregoing process is in general quite applicable to oxide mixtures containing high percentages of cerium. Malaguti⁽²⁶⁾ in contrast to Weiss and Geiger⁽²⁷⁾ found the 'active' oxygen in cerium oxide could be titrated by H_2O_2 in the presence of nitric or sulphuric acids and that the active oxygen in praseodymium oxide could be similarly determined by titration with ferrous sulphate. It is found, however, that in the presence of other rare earths much lower accuracies are obtained by this method than by that already given. Wolf *et al.*⁽²⁸⁾ have suggested a gasometric determination of the 'active (praseodymium) oxygen' based upon evolution of oxygen when the oxide is dissolved in nitric acid.

In determining rare earths, *in toto*, both gravimetric and volumetric methods may be applied, although the former are more common. From simple solutions, or such as are obtained after separation of, for example, heavy metals by mercury cathode, the rare earth group may be precipitated as oxalate, hydroxide, oxinate, cupferrate, etc., and the precipitate obtained ignited to oxide. Some considerations of the quantitative nature of such precipitations have already been made and, whilst it is clear that several limitations apply to such gravimetric methods, with due attention to precision adequate results can be obtained. It would seem worthy of note that Kuznetsov *et al.*⁽¹⁹⁾ agree that, without a coprecipitant, the rare earths as a group are incompletely precipitated as hydroxides or oxalates from solutions more dilute than $1 : 10^5$. These workers recommend that where concentrations more dilute than this are being examined, organic precipitants be employed such as arsenazo, stilbazo, etc. From dilutions of $1 : 10^9$, 93 per cent precipitation is claimed at pH 5–7.

For general purposes, however, precipitation of the rare earths as a group can be considered readily effected by more simple procedures.

Oxalate precipitation. The rare earth solution should contain *ca.* 1 g oxides in 150 ml of solution, preferably as nitrate, and no more than 5 per cent free acid. Heat the solution to 80°C and add slowly, with strong agitation, 80 ml of saturated oxalic acid solution. Control the rate of addition so that the temperature drop is not more than 5°C . Allow the oxalates to settle and cool overnight, then filter through a Whatman 540 paper or its equivalent. Wash the precipitate with 2 per cent oxalic acid solution. Transfer to a weighed crucible and ignite, gently at first, and then at 800°C for 30 min. Cover the crucible whilst it is cooling and weigh quickly to avoid error due to absorption of moisture and carbon dioxide from the air.

Hydroxide precipitation. The rare earth solution should contain not more than 0.5 g in 100 ml of solution. If cerium (4+) is present reduce with one or two drops of hydrogen peroxide, or hydrazine. Heat the solution to 80°C and add a few drops of phenolphthalein indicator solution. Add slowly, with stirring, ammonia solution (1:4) until the indicator changes colour. Allow to cool and the hydroxides to settle, and filter through a coarse filter (Whatman 541) washing with 1 per cent ammonia solution. Ignite finally at 800°C, cool and weigh as above.

As has been stressed before, appreciable losses of scandium will be encountered in oxalate and hydroxide precipitations. Where this element is expected to be present, other gravimetric methods must be applied (*vide supra*).

Since precipitation of the rare earths by oxalate obviously produces a change in conductivity of the solution, it has been suggested that potentiometric titration with oxalate ions be carried out⁽³⁰⁾. Platinum/calomel, antimony/antimony oxide, etc., electrode systems have been suggested as appropriate and, in oxalate precipitations, equivalence points are reached at 30–170 mv, depending upon temperature of the solution and the nature of the rare earth species present.

Through recent years the use of chelating agents in volumetric analysis (chelatology) has received remarkable impetus through the development of methods employing ethylenediamine tetra acetic acid ('enta' or EDTA) as the titrant. The principles underlying such titrations have been excellently expounded by Schwarzenbach⁽³¹⁾, but we are here concerned only with the applications of these principles to analysis of total rare earths. Although chelation with EDTA has been much employed in separations of individual rare earths⁽¹⁾, in chelatology it is applicable only as a group titrant. The principle of its application may be simply stated. If, to a rare earth solution, there be added a chelating agent (EDTA), complexes are formed in which the rare earths lose their ionic character and no longer react to those reagents which evoke ionic response. For example, in simple ionic solution the rare earths may be precipitated as oxalates or hydroxides. In complexed solution with EDTA such precipitation does not occur. If again, therefore, we add to the rare earth solution a dye or reagent which produces a coloured complex with the free ions, the colour thus produced will be discharged at the point at which all rare earth ions in solution have been converted to the complex form (sequestered). Several dyes have been suggested as indicators for such titrations and in the specific instances of the rare

earths the following have been found useful: Eriochrome Black T⁽³²⁾, Thorin⁽³³⁾, PAN⁽³⁴⁾, and Xylenol Orange⁽³⁵⁾. Several variants upon these dyes have also been suggested⁽³⁶⁾.

The endpoint of a complexometric titration can also be detected by the changes which occur in pH at equivalence points. If the slightly acid (pH5) solution of the rare earths be titrated with a solution of, e.g. the sodium salt of EDTA, a pH increase will be easily detected at the equivalence point. This method has, however, the disadvantage that the solution has to be neutralized carefully before the titration and, since the pH jumps occur above pH *ca.* 7, they are influenced by the presence of carbon dioxide.

A third titrimetric procedure which can be applied is again dependent upon the pH effect attendant upon complex formation. The solution of rare earth elements is adjusted to pH *ca.* 5-6 and to it is added a solution of the chelating titrant at a pH of *ca.* 6-7. The mixture shows a lower pH than the constituents because of the hydrogen ions produced by the complex reaction in proportion equivalent to the amount of the metal present. The hydrogen ions released in this way can then be titrated alkalimetrically or, by adding a mixture of iodide and iodate ions, iodine, equivalent to the metal titrated, is liberated and can be titrated in the usual way with thiosulphate.

Although the technique of chelatometric titration is no more difficult than normal acid-base titrations, attention to detail is required, and for this reason reference should be made to original papers and bibliographies⁽³⁷⁾ for details of procedures to be followed in applying this technique to analysis of the rare earths.

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CHAPTER VI

SPECTROPHOTOMETRY

THERE ARE two basic methods for spectrophotometric analysis of the rare earths. One utilizes the band absorption spectra of the coloured ions and the other is based upon the absorption spectra developed by the formation of coloured dye complexes. A variation on the first method, however, is that, more utilized for the determination of traces of rare earths, in which the band absorption spectra of rare earth ions are enhanced by complex formation.

Those members of the rare earths group which yield coloured compounds with uncoloured anions (oxide, nitrate, chloride, sulphate, etc.), exhibit, in solution, band absorption spectra in the visible or near visible regions (350–750 $m\mu$). These spectra differ markedly from those of coloured salts of other elements except those of the transuranium series insofar as they present a few, well defined, and highly characteristic bands instead of continuous, or semi-continuous, absorption over several hundred Angstroms. Although the origins of these precise absorption bands are only incompletely understood, it is accepted that they arise in general from electronic transitions involving the 4f orbitals. Normally forbidden, these transitions are permitted by electric dipole effects⁽¹⁾.

Figure 6-1 (after Prandtl and Scheiner⁽²⁾) shows the absorption spectra of the various rare earth ions. It will be noted that, through the lanthanon series, there occurs a general drift of absorption peaks towards the ultraviolet as far as gadolinium, the trend being then reversed. This trend is, to some extent, paralleled by rare earth emission spectra (*vide* Chapter VII) and bears some relation to the gradual filling of the 4f orbital, a stable, midway, atomic configuration being obtained with seven electrons. Spectra for scandium, yttrium, lanthanum, promethium, ytterbium and lutetium are not shown; the first three and lutetium have no absorption spectra in the visible or near visible whilst that of ytterbium is confined to the near infra red, beyond the boundaries of the Figure. Promethium has been shown to

have an absorption spectrum similar to that of neodymium⁽³⁾ but, because the average analyst is unlikely to encounter this element in his work, its appearance is not noted here.

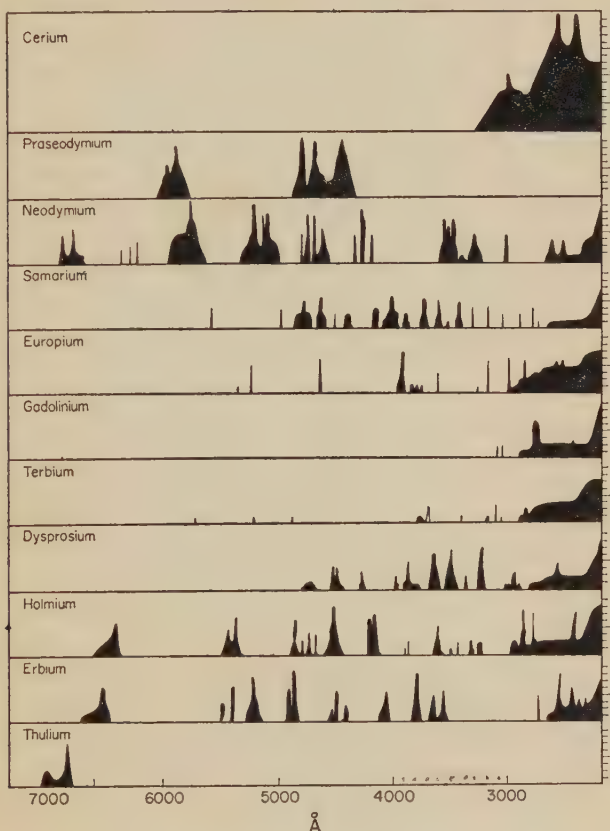


FIG. 6-1. Absorption spectra of rare earth ions (after Prandtl and Scheiner). Chloride solution of 1, 0.5, 0.25, 0.125 (g.atom/l.). Solution depth 50 mm.

It will be seen that the levels of energy absorption through the lanthanon series are such that only about one half of them display absorption in the visible range — Pr, Nd, Sm, Dy, Ho, Er. Instrumental methods, however, permit observation of the spectra of those elements shown in the Figure, and of ytterbium.

Because the absorption spectra of the rare earths is, in general, attributable to energy absorption by the low-lying 4f transitions, it could be postulated that the position and shape of the bands would be unaffected by ions associated with the absorbing rare earth ions. It should be expected that such association could influence only the outer (5*d*, 6*s*) valence shells. But this is not so. The absorption spectra observed in simple aqueous solutions are those of the aquo-solvated rare earth ions and replacement of the hydration sphere, whether it be partial or total, upon e.g. complex formation, or association with an anion or non aqueous solvating molecule, grossly perturbs the low-lying orbitals. This perturbation is demonstrated by variations in absorption wavelength and structure of the absorption band⁽⁴⁾ (Fig. 6-2). Analytical techniques based upon absorption spectra of the rare earths must therefore always be standardized by prior calibration of the spectrophotometer used against rare earth solutions as ionically simple as possible. The presence of, e.g. carboxylic acids, is to be strictly avoided in rare earth solutions intended for spectrophotometry. Although organic anions undoubtedly have the greatest effect upon rare earth spectra, inorganic anions are also influential. In this latter instance waveband shifts and extinction coefficient variations are usually too slight to have much effect upon analyses although phosphate ions have a gross effect and must be eliminated.

Few studies have been made of the effect of cations upon rare earth absorption bands except where the cations also exhibit absorption and here adequate correlation can be applied where the interference extinction coefficients are known. Probably the most disturbing cations — other than those of the other rare earths — are uranium, iron, copper, chromium, nickel, manganese, vanadium, etc., and the transuranium elements. In most analyses these interferences can, and should be, reduced to ineffective proportions by suitable separation techniques before spectrophotometry.

Visual observation of rare earth absorption spectra through optical spectrometers of low dispersion can give an indication of the composition of a mixture but, even after much visual practice, the personal error is too great for such observations to yield more than qualitative evaluation.

Several techniques of rare earth analysis, based upon their absorption spectra, were suggested by earlier workers⁽⁵⁾. Before the advent of the spectrophotometer, direct visual spectrometric comparison on

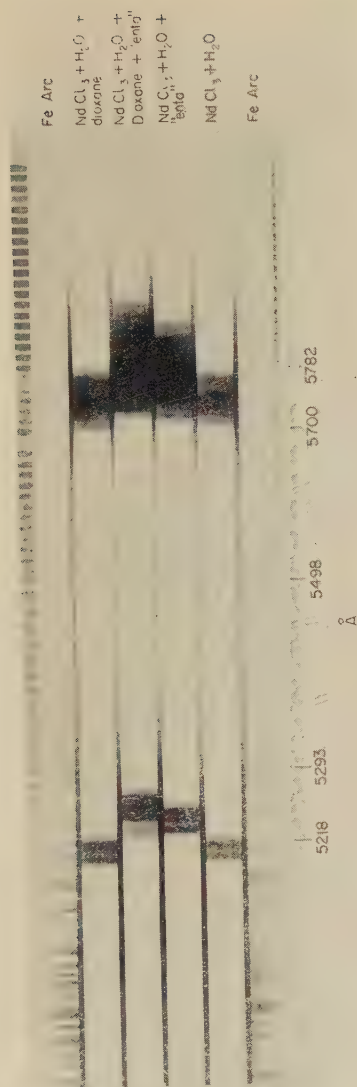


FIG. 6-2. Perturbation of Nd³⁺ absorption spectrum under solvent and chelate influence.

the Nessler principle was first employed, supplemented in the ultra-violet by photographic techniques. Yntema⁽⁶⁾ suggested a method of analysis consisting of finding the dilution necessary to effect disappearance of the most persistent band of a given rare earth in a mixture under rigid photographic conditions. The original concentration was then calculated from that of a pure rare earth solution which likewise just failed to give the same band under identical conditions. Friend and Hall⁽⁷⁾ redetermined the accuracy attainable by the visual Nessler procedure, and the toleration concentrations of free nitric acid and the nitrates of cerium and magnesium which may be present without appreciably affecting the results. When a 6 cm absorption cell was used, neodymium and praseodymium nitrates could be estimated separately in solutions of 3–4 per cent concentration with an accuracy of about 1 per cent by comparing the intensities of suitable absorption bands with those of standard solutions. Toleration limits found for nitric acid, magnesium, sodium, cerium and lanthanum nitrates were of the order of 5–8 per cent. In the presence of neodymium, praseodymium could not be estimated in this way; but the former could be readily estimated in presence of up to 50 per cent of the latter. Streden⁽⁸⁾, making similar studies of chloride solutions, found an accuracy of ± 1 g/l. at 10 g/l. concentration, but this decreased to ± 5 g/l. at the 100 g/l. level.

Although Rodden and Partridge⁽⁹⁾ were unable to obtain, with a filter photometer, accurate results for praseodymium analyses, Marsh⁽¹⁰⁾ satisfactorily applied such instrumentation to determinations of neodymium and praseodymium.

When Ilford 606 and 607 filters were used together, concentrations of praseodymium from 0–100 g/l. could be estimated within ± 2 g/l. Neodymium analyses in the same concentration range were accurate to 1 g/l. when the 604 filter was used alone. Neodymium interferes slightly with the estimation of praseodymium and, when both are present in a solution, 3 per cent of the neodymium reading must be deducted from that of praseodymium before calculating the latter's concentration.

The increasing application of monochromatic spectrophotometry has tended to obscure the analytical value of the simpler filter photometer. Although dispersion of the latter type of instrument is relatively low, and such instruments are dependent upon filters for wavelength definition, the very mode of wavelength selection tends to nullify the

effects of complexing anions, and spectrum-disturbing cations which adversely affect spectrophotometric work.

Analysis of the rare earths by absorptiometry using a monochromatic spectrophotometer was first proposed by Rodden⁽¹¹⁾ who summarized absorption spectra, measured with a Coleman Model 10S instrument, for rare earth nitrate solutions from 3500 to 10,000 Å. Spectral transmissivity curves were obtained showing that, for concentrations up to 10 mg/ml, the absorbency of neodymium solutions follows Beer's Law. Above this concentration the law was said to be invalid. Absorption by both praseodymium and samarium was found to be non-linear with concentration. Limits of detection for praseodymium and samarium (402 mμ) were 1 and 3 mg/ml respectively. The limit of detection of neodymium varied according to the wavelength of the absorption band used for the determination. At 521 mμ, 1.5 mg and at 798 mμ, 0.5 mg were detectable.

The only spectral absorption band which Rodden found applicable for the determination of praseodymium in mixtures was that with minimum transmittancy at 446 mμ. Neodymium and samarium interfered at 469 mμ and 590 mμ, some interference by samarium occurred also at 446 mμ. For determination of neodymium the 798 mμ band was that most preferred and sensitive. Analysis for samarium could be made at 402 mμ only because the absorption at 949 mμ is somewhat low, and praseodymium and neodymium interfere at 479 mμ. Europium seriously interfered in the spectrophotometric determination of samarium.

In a study of absorption spectra of the heavy lanthanons, Rodden obtained transmittancy concentration curves for Dy, Ho, Er, Tm, and Yb, employing the absorption bands at 910, 643, 521, 684, and 950 mμ respectively. Removal of cerium from such systems is, however, necessary. Beer's law holds for absorbancy of these heavy rare earths and the detectable limits in 10 ml are:

Dy	12.5 mg	908 mμ
Ho	12.5 mg	643 mμ
Er	20.0 mg	379 mμ
Tm	25.0 mg	683 mμ
Yb	20.0 mg	975 mμ

The general applicability of Rodden's work was confirmed by several similar studies⁽¹²⁾, and subsequently amplified by Moeller and

Brantley⁽¹³⁾ and Wylie⁽¹⁴⁾. A general development of these later workers was the use of extinction coefficients instead of calibration graphs, and, in general, accuracy was improved to the order of $\pm ca.$ 1 per cent. The continued work confirmed to a high degree the absorption spectra obtained by Prandtl and Scheiner (*loc. cit.*), although some of the weaker bands observed by these workers were not found in later work because of instrumental limitations.

Spectra for chloride, nitrate, acetate and perchlorate solutions of the rare earths were found to be essentially similar although nitrate ions obscured rare earth absorption below 3400 Å. The similarity of absorption of acetates would appear to be one of kind only since displacement of bands towards longer wavelengths was found. Subsequent work by Vickery⁽⁴⁾ has confirmed this displacement. Absorption by erbium ions presented some anomalies; chloride solutions gave only non-reproducible results but perchlorate solutions were quite stable. Gadolinium solutions, when examined under normal operating conditions, showed only broad diffuse absorption at 2730 Å. With more precise instrumentation, albeit with loss of sensitivity, the broad absorption was resolved into six relatively sharp bands. Subsequent work⁽¹⁵⁾ further resolved the gadolinium U.V. absorption spectrum into 18 absorption peaks and two definite inflexions between 2400 and 3150 Å.

Within general limits (exceptions being noted below), it is now accepted that absorption bands of the rare earth metal ions adhere to Beer's law. Absorption coefficients may therefore be obtained from the Beer-Lambert expression

$$K = \frac{\log I_0/I}{cl}$$

where c = concentration of metal in g/l.

l = light path

I_0 and I = intensities of incident and transmitted light respectively.

If c be given in moles/litre, the expression derives the molar absorption coefficient (ϵ).

Moeller and Brantley (*loc. cit.*) found that excess of chloride ion had no measurable effect upon absorption by the light lanthanons, but that the heavy earths were sensitive to such conditions. It may be taken therefore that spectrophotometric analysis is best conducted in perchlorate solutions. Wylie (*loc. cit.*) confirmed the effect of

nitrate ion upon the rare earth absorption spectra, finding free acid to cause a decrease in intensity of certain bands and an increase in that of others. In general, solutions containing mixed anions, and anything but the smallest amount of 'neutral' salts should be avoided.

Moeller and Brantley considered mutual effects of lanthanon ions upon each other's absorption to be negligible, except for an increase in the absorption values for erbium when ytterbium or thulium was present. In somewhat more concentrated solutions, however, Wylie found the intensity of the samarium 402 $m\mu$ band to be enhanced by the presence of lanthanum and/or neodymium. The degree of enhancement appears to depend upon not only the total concentration of these ions, but also upon the ratio of their concentration to that of samarium. Spectrophotometric determination of samarium in the presence of high concentrations of the lanthanons may therefore lead to high results. This is similar to the observations of Quill *et al.*⁽¹⁶⁾; Marsh, however (private communication), has found the absorption of traces of Sm in Nd nitrate to follow Beer's Law although the band peaks shift by 10–15 Å.

There is some disagreement about selection of the most suitable absorption bands for spectrophotometric analysis between workers in this field. Thus, Spedding *et al.*⁽¹⁷⁾ prefer the 740 and 795 $m\mu$ bands for neodymium determination, whilst Moeller and Brantley consider the 521.8 band more applicable and Banks and Klingman⁽¹⁸⁾ the 575 band. Again, Holleck and Hartinger⁽¹⁹⁾ and Banks and Klingman (*loc. cit.*) employ the 523 $m\mu$ band for erbium — Moeller and Brantley use the 394 band. Table 6-1 gives extinction coefficients for the rare earth ions at varying wavelengths and under varying conditions. The author's preferred wavelengths are marked therein by asterisk.

From the extinction coefficients given in Table 6-1, and the observed optical density of the solution, rare earth metal concentrations are readily calculated on the basis of the Beer-Lambert equation. Since $\log I_0/I$ is read directly as optical density, and l commonly = 1 cm,

$$c(\text{moles/l.}) = \text{Optical density}/\epsilon$$

Correction for interfering elements is applied by multiplying the interference ϵ by the concentration of interfering element (obtained at its appropriate wavelength) and deducting the product from the

TABLE 6-1. PARAMETERS FOR SPECTROPHOTOMETRIC ANALYSIS OF RARE EARTHS

Element	Anion	Wavelength (mμ)	Slit width (mm)	ε	Interference ε	Limit of detecton	Ref.
Pr	ClO ₄ ⁻	444	0.02	10.34	Nd (0.021) Sm (0.142) Er (0.300) Ho (0.454) Er (0.306)		25
*		444.2	0.02	10.49			18
	Cl ⁻	444	0.049	10			14
				7.3			12
			0.04/0.05	10.5			19
*		444.2	0.049	10.2			14
		444.5	0.025	9.85	Sm (0.160)	0.143 g/100 ml	13
		466.8	0.04/0.05	4.64			19
		481.9	0.04/0.05	3.99			19
	NO ₃ ⁻	444	0.049	9.30			14
		444.5	0.025	9.20		0.165 mg/100 ml	13
Nd *	ClO ₄ ⁻	521.8	0.013	4.3		0.336 g/100 ml	13
		575	0.025	6.93	Pr (0.082) Pr (0.102) Tm (0.579) Er (0.143) Dy (0.034)		25
*		575.5	0.02	6.93			18
		794	0.02	11.78			
	Cl ⁻	346.5	0.04/5	3.71			18
		350.4	0.04/5	2.91			19
		353.8	0.04/5	5.12			19
		512.2	0.023	1.73			14
		520.7	0.04/0.05	4.51			19
		521.8	0.013	4.33		0.333 g/100 ml	13
		522	0.023	4.33			14
		575.2	0.04/0.05	7.11			19
		734	0.04/0.05	6.76			19
		741	0.01	6.80			14
				6.13/6.27			12
		784	0.04/0.05	9.11			19
		796	0.01	9.65			14
		853	0.04/0.05	3.57			19
	NO ₃ ⁻	512	0.023	1.17			14
		521.8	0.013	3.88	Er (1)	0.372 g/100 ml	13
		522	0.023	3.87			14
		741	0.01	6.40			14
		796	0.01	9.65			14
Sm	ClO ₄ ⁻	401	0.04	3.26	Pr (0.019) Nd (0.012) Dy (0.187) Eu (0.097)		25
*		401.5	0.04	3.31			18
	Cl ⁻	401.6	0.04/0.05	3.49			19
		402	0.044	3.12	Eu (0.08)	0.48 g/100 ml	13
			0.073	3.11			14
	NO ₃ ⁻	402	0.044	3.28		0.458 g/100 ml	13
			0.073	3.24			14
Eu *	ClO ₄ ⁻	394.2	0.04	3.06	Dy (0.233) Sm (0.148)		18
	Cl ⁻	298	0.04/0.05	1.38			19
		317.9	0.04/0.05	1.26			19
		393.9	0.029	2.92	Sm (0.15)	0.52 g/100 ml	13
		394.3	0.04/0.05	2.72			19
	NO ₃ ⁻	394.5	0.053	2.05		0.743 g/100 ml	13
Gd *	Cl ⁻	272.8	0.205	2.34		0.67 g/100 ml	13
		272.9	0.04/0.05	3.53			19
		273.7	0.04/0.05	1.75			19
		273.8	0.205	1.15			13
		274.1	0.205	1.48			13
		275.4	0.205	1.49			13
		275.6	0.04/0.05	2.51			19
			0.205	2.11			13
		276.3	0.205	0.97			13
Dy *	ClO ⁻	908	0.02	2.46	Ho (0.113) Yb (0.089)		18
	Cl ⁻	350.4	0.04/0.05	2.44			19
		364.9		1.96			19
		805		1.57			19
				1.80			11

TABLE 6-1—continued

Element	Anion	Wavelength (mμ)	Slit width (mm)	ε	Interference ε	Limit of detection	Ref.
Ho	ClO ₄ ⁻	905	0.04/0.05	2.15	Er (0.076) Er (0.153)	0.419 g/100 ml	19
		537	0.02	2.73			11
		640.4		5.16			18
		450.3	0.04/0.05	3.53			18
	Cl ⁻	536.8	0.04/0.05	3.80			19
			0.04/0.05	4.26			19
				2.75			11
		640.7	0.04/0.05	2.80			19
Er	ClO ₄ ⁻			2.40	Nd (0.0164) Eu (0.299) Dy (0.252) Nd (1.68) Ho (0.076) Nd (0.0164)	0.419 g/100 ml	11
		379	0.040	6.82			25
		379.2	0.030	4			13
		379.6	0.02	7.18			18
	Cl ⁻	523.5	0.02	3.2			18
				6.82			25
		379.4	0.04/0.05	5.59			19
		523		3.04			19
Tm	ClO ₄ ⁻	652.5		1.68	Nd (0.48) Nd (0.336)	0.68 g/100 ml	19
		682.5	0.018	2.49			13
		683	0.02	2.56			18
		682.5	0.04/0.05	2.52			19
	Cl ⁻		0.018	2.58		0.659 g/100 ml	13
				2.34			11
		774	0.04/0.05	1.07			19
		974	0.02	2.12			18
Yb	ClO ₄ ⁻	975	0.026	1.96	Er (1.29) Er (1.42)	0.885 g/100 ml	13
		967.5	0.04/0.05	1.90			19
				2.34			11
	Cl ⁻	975	0.026	1.94		0.901 g/100 ml	13
				1.91			13
		975	0.026			0.912 g/100 ml	13

observed optical density of the element being determined, then putting the corrected optical density into the above equation. Stewart and Kato⁽²⁰⁾ employ a correction factor which is essentially the product referred to, and is actually the ratio between the extinction coefficient of the interfering ion's spectrum at the index peak of the element of interest, and the extinction coefficient of the interfering ion's own primary index peak.

Because results obtained are in terms of concentration of metal ion, conversion to terms of chloride, perchlorate, etc., is sometimes required. Conversion tables for this and other purposes will be found in Appendix II.

Manipulative techniques in simple 'band' spectrophotometry require in general, little more than strict attention to accuracy of dilution and cleanliness. A known weight of sample is preferably obtained in perchlorate solution and diluted with distilled water in a volumetric flask. 10 ml of the solution are pipetted into a centrifuge tube, balanced against water and spun at a high speed for several minutes.

The spectrophotometer cells — preferably of quartz — are main-

tained clean by overnight immersion in chromic acid solution followed by much flushing with distilled water. When not in use during the daytime, the cells should be kept in distilled water. Before use, the outer surface of the cell should be dried by blotting on lintless absorbent paper. The cells should be held only by the unpolished sides and not stroked on the paper but simply placed into contact. Final cleaning and polishing of the optical surfaces is done with well-washed chamois leather.

After centrifuging, 2 ml of supernatant solution are withdrawn from the tube by pipette, and used for washing out the inside of the optical cell. After shaking out this wash liquor, the cell is inverted for a few moments on bibulous paper and then filled to within a small distance from the top with about 6 ml of the solution. Covers should always be employed on the cells and the optically finished surfaces should never be touched with the fingers or forceps. Loading of the cells into the carrier should never be attempted without removing the carrier from the instrument slide.

Wylie's practice of centrifuging solutions before measurement is to be highly recommended. Several workers have noted the apparent increase in intensity of absorption lines of, for example, neodymium when adsorbed upon silica, alumina, etc.⁽²¹⁾ and we might expect a similar effect to be found in analytical solutions which have not been centrifuged. Centrifugation further serves to remove extraneous opacity of the solution which also tends to give high absorptivity values.

Instrumentation procedures vary with instrument manufacture and are therefore difficult of explication in the same manner as chemical procedures; attention in this instance must be paid to manufacturers' instructions. Some operational characteristics are, however, applicable to all types of spectrophotometer and for these the following indications can be given.

Although complete resolution of a waveband is desirable, this is not essential so long as the slit width employed for analysis is the same as that employed in determination of the extinction coefficients. It must be remembered, moreover, that instrumental response to the spectra of europium, erbium, samarium and gadolinium is much affected by changes in slit width. Wylie (*loc. cit.*) recommends adopting the smallest possible slit width consistent with adequate sensitivity and then, since significant changes may occur in observed

optical density with small errors in wavelength setting, bring the wavelength scale as close as possible to the desired wavelength, locating the exact position of the bandhead by noting the position for minimum photo-cell response. Slit-widths should be approached from one direction only (larger to smaller slits) to avoid the mechanical backlash noticeable at very small slit widths. In gadolinium analyses, a hydrogen lamp and fixed slit width of 0.1 mm are employed the instrument being zeroed at 272 m μ with gadolinium solution in the cell. The wavelength is then altered to 272.6 m μ and the optical density measured together with the appropriate corrections for the presence of the other rare earths.

The tedious, but most accurate, practice with manually operated spectrophotometers of taking a number of readings around an index peak position, is obviated by the use of recording devices. Stewart and Kato (*loc. cit.*) have examined the advantages attendant upon the use of a recording spectrophotometer (Beckman DK) and have found the additional advantage that not only can a full scan readily be obtained, but that the analyst is also, thereby, made aware of the presence, and effect, of unsuspected absorbing ions. Where these latter are other rare earths, corrections for their absorption are more easily applied than hitherto.

Very few absorption peaks would be free from interference in the usable spectrum if a mixture containing all the rare earths were examined, but this is rarely the case. Interference between the light lanthanons as a group is relatively minor and easily adjusted. Spectrophotometry of the heavy lanthanons is more of a problem because of the large number of mutual interferences. Europium has but one usable peak and this is free from interference except from a samarium band close by. Dysprosium shows several acceptable peaks if only heavy earths are present in a mixture but, in the presence of the complete group only the bands in the near infra red are usable — especially that at 911 m μ . Erbium has an excellent band at 523.5 m μ if no neodymium be present — otherwise gross interference occurs. Determination of a small amount of ytterbium in the presence of a large amount of erbium is extremely difficult because of the proximity of bands. The ytterbium-dysprosium peaks are mutually interfering.

An interesting facet of Stewart and Kato's work is their suggestion for preferred order in which primary index peaks of absorption should be examined to avoid the necessity of applying a series of successive

approximations in computing the corrections. The order suggested is

- | | |
|--|---------------------------|
| 1. Neodymium (575.5 $m\mu$ – ignoring the Pr correction) | 6. Ytterbium |
| 2. Thulium | 7. Samarium |
| 3. Erbium | 8. Europium |
| 4. Holmium | 9. Praseodymium |
| 5. Dysprosium | 10. Terbium (219 $m\mu$) |

Although Stewart and Kato have indicated that absorption bands in the near infra-red adequately may be applied to analysis, this approach has been but little investigated. Instead, more interest would appear to have been paid to the ultra-violet spectra of the rare earths. For determination of gadolinium and terbium this is somewhat of a necessity, and for cerium very applicable. The absorption spectrum of gadolinium shows a group of very narrow bands in the 270–280 $m\mu$ region, terbium has a significant peak at 219 $m\mu$ which can be used for its determination although subject to some interference from cerium, praseodymium and europium. Ceric ions in sulphate solution show broad absorption with a maximum at 316 $m\mu$ but no absorption above 480 $m\mu$. Cerous ions were stated to show maxima at 233, 240, 254, and 256 $m\mu$ ⁽²²⁾. Gordon *et al.*⁽²³⁾ found slightly different values (212.1, 223, 240.4, 253.6, and 295 $m\mu$) but used the 253.6 band for determination of cerium. The 295 $m\mu$ band is sulphate dependent but, in 1 N sulphuric acid the 253.6 $m\mu$ band has a molecular extinction coefficient of 685 and excellent results can there be obtained. Ceric ions must first be reduced with peroxide, and europium, and lanthanum should also preferably be absent (100 mg/l. give 3 per cent error on 80 mg Ce/l.). Nitrates and uranyl ions must also be removed. From Hure and Schonberg's figures⁽²⁴⁾ it would seem that as little as 1–5 γ Ce/ml might be detected by this technique.

Hitherto, spectrophotometric methods of analysis have been based upon absorption of rare earth solutions at given wavelengths relative to the absorption of water as the standard light path. Banks *et al.*⁽²⁵⁾ have, however, shown that differential methods can be applied using rare earth solutions as standards. Such a technique gives a standard deviation of 0.17 per cent, and a significant increase in precision was noted over that obtained by ordinary spectrophotometry. For adequate consideration of the data and procedures presented, reference should be made to the original paper.

As has been indicated, the formation of rare earth complexes in solution leads in several instances to variation in structure of the absorption spectra⁽⁴⁾. Because enhancement of absorption is one of the phenomena observed, it would appear that, in spectrophotometry, employment of such ionic complexes would permit detection and determination of smaller amounts of rare earths than is possible in simple ionic solutions. This premise was examined by Moeller and Brantley⁽²⁶⁾ with specific reference to the absorption spectrum of neodymium complexes with EDTA. At the 576 m μ band extinction was increased by a factor of 1.45 so that, because at this wavelength normal sensitivity is 0.033 g/l., observation of the complexed ion permits a sensitivity of 0.023 g/l. There would appear extant no further work in this area, but the indications given would seem to warrant a deeper study of its implications in the general field of rare earth analysis.

From enhancement of single band intensity by chelate formation, we consider now another application of complex formation to spectrophotometric determination of the rare earth elements. Several dye compounds which absorb light over specific wavelengths also form coloured complexes with rare earth ions, and these compounds generally absorb light at different wavelengths than does the original dye. We have, therefore, what is essentially the development of an absorption due to the rare earth-dye complex. It has not so far been shown that such absorption is specific for any particular one of the rare earth elements but, when only one of these is present, e.g. lanthanum, in small quantities, use can be made of this colour development in establishing a spectrophotometric method of analysis. It may be taken that most interest has developed in the application of this technique to analysis of the non-coloured ions or those in which band absorption is too meagre to be applied at low concentrations. Holleck *et al.*⁽²⁷⁾ made a concise survey of such complex colorimetry of the rare earths.

Cerium peroxy compounds have been variously suggested as suitable media for analyses but, Conca and Merritt⁽²⁸⁾ found that spectrophotometric determination of cerium in simple potassium carbonate solution avoided the difficulties introduced due to flocculated colloids when determinations are made in alkaline solutions with hydrogen peroxide. Using their technique, quadrivalent cerium may be determined by measuring the absorbency in 3 M K₂CO₃

solution at pH 11–12. The optimum range of determination was found to be 2–25 ppm of cerium and accuracy was in general ± 0.2 ppm.

Procedure: Dissolve the cerium material in 0.5 M H_2SO_4 to give a final cerium concentration of *ca.* 0.001 M and oxidize all cerium to the quadrivalent state according to the method of Medalia and Byrne.⁽²⁹⁾ Dilute aliquots of the solution, equivalent to *ca.* 0.5 mg Ce, to 50 ml with 3 M potassium carbonate and measure absorbancy at 305 $\text{m}\mu$ against 3 M K_2CO_3 .

The absorption spectrum of a solution of quadrivalent cerium in potassium carbonate solution is nearly identical with that of a solution which also contains peroxide. Although the extinction coefficient of the peroxy complex is higher than that of the carbonate complex above 380 $\text{m}\mu$, no advantage is offered by the peroxide complex in the region of maximum absorption. A calibration graph is usually employed for this determination and, although several elements interfere, in most cases they are easily eliminated before determination of cerium.

Babko and Eremenko⁽³⁰⁾ attempted to improve the sensitivity and accuracy of the peroxide-carbonate technique by the addition of EDTA and glycerol at pH *ca.* 9, but their attempts were not entirely successful and interferences were not removed. It would appear therefore that such techniques have nothing to offer over the Ce^{3+} absorption technique promulgated by Gordon *et al.* (*loc. cit.*). The absorption of sodium cerimolybdate at 380 $\text{m}\mu$ has been recommended by Shakova and Gairilova⁽³¹⁾ but the sensitivity of the procedure is low and interferences high.

Because of the desire for a coloured complex of the uncoloured earths, much attention has been paid to the iodo compounds of the basic rare earth carboxylates⁽³²⁾ but, except in singular systems, the colour produced would seem to be an attribute of the rare earths as a group. Specific attention was paid by Moeller and Quinty⁽³³⁾ to the possible analytical use of the 'lanthanum blue' iodoacetate compound. Despite adherence of absorption at 580 $\text{m}\mu$, to Beer's Law, too many solution variables would appear to influence reproducibility of absorption data to render this approach adaptable to accurate analysis.

More success has been obtained with the Alizarin Red S compounds by Rinehart⁽³⁴⁾ and Eberle and Lerner⁽³⁵⁾. Accuracy of *ca.* 3–5 per

cent can be obtained in the absence of interfering ions by application of the customary acetate-buffered technique, and quantities of the order of 10 to 120 γ rare earths can be detected and determined.

Procedure: Obtain up to 150 γ rare earths in about 3 ml of slightly acid solution. Adjust with 0.2 M NaOH to phenol red and then return the colour to yellow with 0.03 M HCl. Add 0.5 ml of ammonium acetate buffer solution and 2 ml of 0.1 per cent sodium alizarin sulphonate solution. Dilute the solution to 10 ml in a volumetric flask, and, after allowing the solution to stand and develop its maximum colour for 5 min determine absorbancy at 550 $m\mu$.

Note

1. Since Eberle and Lerner prefer to use the 520 $m\mu$ wavelength for absorbance readings, it is probably preferable to establish the peak of absorption and calculate the rare earth concentration from a calibration graph.

Where the rare earths as a group (or individuals) can be precipitated from solution as organo-soluble complexes, such solutions can usually be employed in spectrophotometric analyses if they exhibit absorption at wavelengths different from that of the complexing agent. Such a technique has been applied to the rare earth 'oxinate' complexes. Precipitation of the oxinate is effected in the customary way, the oxinate is dissolved in, for example, amyl acetate, chloroform, etc., and the absorption measured. Here again, wavelengths of maximum absorption vary for each of the rare earth elements, and this has to be determined individually. Alimarin *et al.*⁽³⁶⁾ have examined the absorption spectra of the quinolate—rare earth complexes and their data would seem to confirm the wavelengths used by the various workers—Westwood and Mayer⁽³⁷⁾ and Misumi⁽³⁸⁾ use 470 $m\mu$ for cerium determination, Murthy *et al.*⁽³⁹⁾ 330 and 340 $m\mu$ for yttrium and Bergstresser⁽⁴⁰⁾ 365 $m\mu$ for lanthanum.

Procedure: To 50 ml of separated rare earth solution containing not more than 10 mg of metal ion, add, in the cold, with constant stirring, 15 ml of 1 per cent solution of oxine in alcohol. Precipitate the oxinate complex by the addition of ammonia solution to pH *ca.* 11. Stir for about 3 min and then extract the oxine complex into 25 ml of amyl acetate. Separate the two phases and dilute the organic phase to 50 ml in a volumetric flask using second and third acetate extractions to adjust the volume. Transfer an appropriate quantity of the solution to a spectrophotometer cell and measure absorption at the appropriate wavelength against amyl acetate as the standard.

Several other chromophoric systems have been suggested at different times as reagents for colorimetric analysis of the rare earths but it must be remembered that, in theory, any singular colour development can be applied to analysis providing that its light absorbency adheres to Beer's Law.

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CHAPTER VII

SPECTROGRAPHY

FOR A long time emission spectroscopy of the rare earth elements has been a difficult subject. Among the many reasons for this difficulty, the most important have been lack of pure materials for study and complexity of the spectral structures evinced. Although the first of these hindrances is now almost surmounted, the latter persists. Upon arc or spark excitation of rare earth compounds a high percentage of ions is produced and the intensity of the lines due to these ions is generally much greater than that of the lines due to unionized atoms, with the result that these latter are rendered even more difficult to observe and measure. Moreover, the very complexity of the rare earth emission spectra, which might be considered characteristic, induces much 'masking' and obscuring of intense lines due to other elements. In spectrography, therefore, as in most areas of rare earth analysis, the preferred procedure is to examine material which has already undergone some form of beneficiation or purification. As will be seen, this treatment forms an important facet of spectrochemical analysis; Rose *et al.*⁽¹⁾ have pointed out, however, that analysis of rare earth concentrates, or conservative systems, is quite a different matter from analysis of naturally occurring rare earth materials or minerals.

A general dissection may be made of the types of rare earth analyses which may be, and are, effected by emission spectrography:

- (a) Rare earths in a non-rare earth matrix. In silicate, etc., matrices analyses are relatively easily accomplished. Transition element matrices present more complex spectra and may give continuous radiation. Systems of this kind are therefore most subject to prior chemical separation.
- (b) Rare earths in a mixed rare earth matrix.
- (c) Minor quantities of rare earths in a 'pure' rare earth matrix.
- (d) Minor quantities of non-rare earths in a 'pure' or mixed rare earth matrix.

After chemical separation, systems of group (a) should be considered as in groups (b) or (d) according to the type of analysis required. We shall mainly be concerned here with (b) and (c) type analyses and, in general the methods applied thereto can be adequately applied to the other group types.

An interesting comparison may be made of rare earth absorption and emission spectra with those of other elements. The absorption spectra of many non-rare earth ions consist of nearly continuous absorption over several hundred Angstroms-absorption spectra of the rare earth ions have been seen to be band-like in nature, none of the bands extending for more than a few millimicrons. Emission spectra of most non-rare earth elements show several intense 'characteristic' lines — rare earth emission spectra in general are highly complex with thousands of lines of uniform intensity so that emission radiation may almost be considered continuous (La, Eu, and Yb, have relatively simple spectra). However, with tables of most persistent lines (Table 7-1), spectrography presents the simplest technique for detection of minor, or trace, quantities of the rare earths. Limits of detection vary somewhat with the basis employed by the worker. Using semi-quantitative methods, Waring and Annel⁽²⁾ determined the following standard sensitivities in 10 mg samples:

0.1 per cent Ce, Sm.

0.01 per cent La, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu.

0.001 per cent Sc, Y.

0.0001 per cent Yb.

McClelland⁽³⁾, however, reports much higher values. In the presence of non-rare earth elements, much judgment must be exercised in selection of the appropriate lines for rare earth detection. When titanium in amounts more than 0.1 per cent is present, its 3242 Å line interferes with yttrium 3242.3 Å. Cerium lines 4186.6, 4040.7 and 4012.4 Å, below a 1 per cent concentration, are masked by cyanogen bands. The cerium line 4222.6 Å is in a clearer part of the spectrum and has a detectable limit of 0.1 per cent. On the other hand, in silicate, aluminium or copper matrices the cerium 4040.7 and 4012.4 lines may be visible below 0.2 per cent depending in part upon the dispersion available in the spectrograph.

Again, unless rare earth matrices free of the suspected rare earths are available, it is difficult to establish whether the presence of spectral

lines at the characteristic wavelengths of persistent lines of the impurity rare earth are really caused by this latter or by very weak lines of the matrix material or both. Much can be done, however, by using the intensity ratios of homologous pairs, and extrapolating the

TABLE 7-1. MOST PERSISTENT LINES OF RARE EARTH EMISSION SPECTRA
(intensities given in parentheses)

Sc 4246.8	Y 4102.38 (150)	La 4086.71 (500)
3911.8	3774.33 (12)	3988.52 (1000)
3907.5	3710.29 (80)	3949.11 (1000)
3369.0	3600.73 (100)	3794.77 (400)
3019.3	3327.90	3790.82 (400)
2552.4	3242.28 (60)	3337.49 (800)
Ce 4572.28 (355)	Pr 4408.84 (125)	Nd 4325.80 (80)
4186.60 (80)	4225.33 (50)	4303.57 (100)
4133.80 (35)	4222.98 (125)	4156.08 (10)
4040.76 (70)	4179.42 (200)	4109.46 (30)
4012.39 (60)	4100.75 (200)	4061.09 (40)
3942.15 (35)	3908.43 (100)	4012.25 (80)
Sm 4424.34 (300)	Eu 4205.05 (200)	Gd 3768.41 (20)
3885.28 (50)	4129.74 (150)	3671.20 (100)
3634.27 (100)	3971.99 (1000)	3646.20 (200)
3609.48 (60)	3930.50 (1000)	3422.47 (80)
3592.60 (40)	3819.66 (500)	3362.24 (150)
3568.26 (40)	2727.80 (300)	3350.48 (150)
Tb 3874.18 (200)	Dy 4211.72 (200)	Ho 4103.34 (400)
3676.35 (100)	4000.45 (400)	4053.92 (400)
3585.03 (15)	3944.69 (300)	3891.02 (200)
3561.74 (200)	3645.42 (300)	3796.73 (20)
3509.17 (200)	3531.71 (100)	3456.00 (60)
3324.40 (70)	3407.80 (150)	3398.98 (40)
Er 4419.60 (20)	Tm 3848.02 (400)	Yb 7699.49 (2000)
4007.97 (35)	3795.77 (250)	5556.48 (1500)
3906.32 (25)	3717.92 (100)	3987.99 (1000)
3692.65 (20)	3462.20 (250)	3694.20 (500)
3499.10 (18)	3425.08 (200)	3289.37 (500)
3372.75 (35)	3362.61 (250)	3107.90 (500)
	Lu 3507.39 (100)	
	3397.07 (50)	
	3359.56 (150)	
	3077.60 (100)	
	2911.39 (100)	
	2615.42 (100)	

observed ratios when samples containing added amounts of the impurity are compared.

Because of their low ionization potentials, the rare earths show the strongest lines of their first two spectra in the visible or near ultra violet regions. Ionization appears to occur, most usually, through removal of one or two of the outermost (6s) electrons, and the spectra of the ionized rare earths consequently contain intense lines resulting from the *s-p* transition. It would seem significant that Rose *et al.* (*loc. cit.*) in following Fassel's technique (*vide infra*), and looking for interference-free lines of suitable intensity for analysis, have found these to be representative of singly ionized ions. M.I.T. tables list 100,000 lines between 2000 and 10,000 Å — only 31523 of these are representative of neutral or singly ionized atoms.

TABLE 7-2. SUMMARY OF SPECTROGRAPHIC PROCEDURES

Author	Elements determined	Excitation	Limits (per cent)	Precision
Azcona ⁽³¹⁾	Gd	d.c. arc	0.1-3	±3 per cent
Fassel ⁽¹¹⁾	Y, Gd	d.c. arc	8-100	±2.5 per cent st. dev.
Fassel and Wilhelm ⁽¹¹⁾	Sm, Eu	d.c. arc	0.1-2	4 per cent st. dev.
Fassel <i>et al.</i> ⁽¹¹⁾	Ce, Pr, Nd, La Ho, Dy, Er, Y, Tm, Yb	d.c. arc	0.05-40	max 6 per cent dev.
Feldman ⁽²⁰⁾	Ce, La, Y	d.c. arc C spark	0.005-1 sensitivity 0.1-25 ppm 0.005-1	max 6.3 per cent dev.
Gatterer and Junkes ⁽³⁾	Eu	d.c. arc		
Hamaguchi ⁽¹⁸⁾	Sc	d.c. arc		
Hirt and Nachtrieb ⁽²¹⁾	La, Ce, Pr, Nd, Sm, Gd, Dy	Cu spark	0.005-5 10-100	max error ±15 per cent
Hopkins <i>et al.</i> ⁽⁷⁾		d.c. arc		±10 per cent st. dev. ±10 per cent
McClelland ⁽³⁾	All	a.c. arc		
Norris and Pepper ⁽⁴⁾	La, Pr, Nd, Sm, Gd, Y	C spark	1-30	max error 5 per cent
Rose <i>et al.</i> ⁽¹⁾	La, Y	d.c. arc	0-60	25 per cent 10 per cent
Russell ⁽³²⁾	Dy, Er, Eu, Gd	d.c. arc	0.12-16	
Scribner and Mullin ⁽³³⁾	Sm, Gd, La	d.c. arc	0.1-10	
Selwood ⁽³⁴⁾	All	d.c. arc	5-50	
Short and Dutton ⁽¹³⁾	Dy, Gd, La, Lu, Y, Yb	d.c. arc	0.1	
Smith and Wiggins ⁽⁹⁾	La	Cu spark	28-42	4.6 per cent av. dev.
Spicer and Ziegler ⁽³⁵⁾	All	d.c. arc	0.0001-0.1	
Waring and Annel ⁽²⁾	La, Ce, Pr, Nd, Eu, Gd, Dy, Yb, Y	d.c. arc	0.001-0.1	max error 10 per cent
Waring and Mela ⁽¹⁷⁾				

Numerous methods have been reported for the emission spectrographic determination of the rare earths, and Norris and Pepper⁽⁴⁾ summarized in table form the salient points of some of these techniques. This has now been extended and amplified in Table 7-2. In general, one has to distinguish between rare earths present as major constituents and those present as trace elements in other

compounds. As has been pointed out in the latter instance, separation and concentration processes play an important part in spectrochemistry. Spitz *et al.*⁽⁵⁾ for example, employed the mercury cathode for removal of interfering elements, precipitated the rare earths as hydroxides, with iron as a carrier, and used uranium and sodium chloride as internal standard and buffer respectively. Although the function of sodium chloride can be disputed, determination of 50 γ rare earths in 1 g sample was claimed. However, this procedure is not always applicable and many variants on the separational theme may be applied before anything approaching perfection can be attained⁽⁶⁾. The analyst should refer to Chapter IV for details of separational techniques applicable to spectrochemistry.

Hopkins *et al.*⁽⁷⁾ evaporated nitrate solutions on graphite electrodes, and excited spectra with a low voltage d.c. arc. Magnesium and zirconium were employed as internal standards but, because of the conditions applied, the results obtained were too erratic to be considered applicable to quantitative analysis. By applying the technique to a sufficiently large number of samples, Gatterer and Junkes⁽⁸⁾ were able to obtain results of statistical, but hardly analytical, value.

Smith and Wiggins⁽⁹⁾ determined empirically the most persistent lines of the rare earth spectra, obtaining good agreement with data obtained by Meggers and Scribner⁽¹⁰⁾. Cyanogen lines in carbon arc spectra tend to mask a number of the most persistent rare earth lines but this can be avoided by using copper or silver electrodes in an 8–10 ampere arc (see also below). The overall weakness of the spectrum thus obtained can be avoided by moistening the rare earth oxide with nitric acid just before excitation, but even so, the method is inadequate for the detection of some rare earths at impurity levels. Suppression of the cyanogen bands by running the arc in a steam atmosphere permitted determination of most rare earths at concentrations of less than 0.1 per cent although as little as 0.0005 per cent Eu was stated to be detectable in samarium chloride in the d.c. carbon arc.

Of the severally suggested procedures, those of Fassell *et al.*⁽¹¹⁾ appear to be most generally applicable to the determination of major constituents in rare earth matrices. In the earliest work reported by these investigators, cerium was employed as an internal standard and an accuracy of 3–4 per cent was obtained by employing a 1:1

mixture of graphite and rare earth oxide, obtaining second order spectra with the d.c. arc at 17.5 amp.

Apart from instrumental precision, the value of spectrographic analysis depends upon the method of standardization of the spectra obtained. In general⁽¹²⁾, three types of standardization can be applied: analysis by homologous lines, employment of an outside standard related solely to the relative densities of lines in comparison with those made under similar circumstances, or analysis with an internal standard. Although grossly affected by minor variations in excitation conditions, film processing, etc., the 'outside' standard technique has been applied with some success by Short and Dutton⁽¹³⁾, who, after applying a separation procedure, were able to determine 0.2 ppm of gadolinium in uranium by this technique. The possibilities of error which arise, however, are too great for this to be considered more than a semi-quantitative technique. In the 'homologous pair' technique, no additional material is added to the sample; instead, a constituent of the matrix is chosen whose spectroscopic characteristics are known. From its spectrum a standard line is taken and there is chosen, for the known standard line and the unknown comparison line, which are to be of equal intensity for a given concentration, lines which are known to have approximately the same excitation conditions so that with a considerable change in arc or spark conditions, any change which may take place in one line intensity, will also take place to the same extent in the other. The choice of pairs for spectral analysis may be made by a study of known standards under varied conditions of arc, and once these pairs have been established it becomes possible to eliminate some of the errors attributable to the 'outside' standard approach^(4, 14).

In the use of an internal standard, intensities of lines in the known and unknown sample are referred to some common line of an extraneous element which remains unchanged in both spectra. This procedure, first developed by Gerlach⁽¹⁵⁾, has been extensively developed by Fassel's group. Correct selection of the internal standard, its concentration and spectral lines, have all been generally emphasized, but the major criteria are that line pairs are selected whose components possess desired equivalent excitation properties, intensities, and proximity of wavelength. Where data on excitation potentials are available this is a valuable mode of comparison. Fassel *et al.* (*loc. cit.*) chose only those line pairs whose intensity ratios

varied by less than 5 per cent with a variation in excitation current from 10–19 amp. In analysis of pure oxides for minor constituents, lines of the major constituent are almost ideal standards where the mixture is not too complex. Care must be taken, however, to ensure non-interference of emission lines of the standard and the element sought. Various added elements have been found to have their idiosyncrasies; the second order strontium lines (used by Norris and Pepper (*loc. cit.*)) have their disadvantages in being subject to self reversal. Kulskaya and Volovenko⁽¹⁶⁾ used zirconium as also did Hopkins (*loc. cit.*) but the refractoriness of this element would appear to lessen its value, even in the instance of scandium determination for which it was used. Waring and Mela⁽¹⁷⁾ employed aluminium as an internal standard, obtaining an accuracy of only 10 per cent, whilst McClelland⁽³⁾, using iron in the same way, obtained similar levels of accuracy. Hamaguchi *et al.*⁽¹⁸⁾ used platinum black (2 per cent) and carbon (300 per cent) for scandium analysis using the line pairs Sc 3613·84 and Pt 3204·0.

Smith and Wiggins⁽⁹⁾ list three problems which present themselves in spectrochemical analysis of the rare earth elements; empirical determination of the most persistent lines for a given type of arc excitation; identification of faint lines coinciding with impurity lines; and, methods for avoiding the 'masking' effects developed by the presence of cyanogen bands in graphite and carbon arc spectra. It is usually insufficient to accept standard wavelength tables for selection of persistent lines since, in recent years, many discrepancies have been found, due no doubt in part to the increasing availability of purer materials for examination. Instead, the analyst is recommended to prepare his own set of standard spectra and to determine from them the most persistent lines as was done by Smith and Wiggins. This procedure also eliminates to an appreciable extent the second problem. Elimination of cyanogen bands can of course be effected by utilizing, e.g. copper, silver, platinum, etc., electrodes (*vide supra*), but each variation will introduce other variables into the picture. On copper electrodes, for example, aluminium, thorium, fluoride and sulphate will produce undesirable results and, where calcium is present, gross interference is noted with the gadolinium lines. Wiggins⁽¹⁹⁾ was able to eliminate cyanogen band 'masking' by surrounding the arc with steam — a simpler procedure using argon or argon-oxygen atmospheres would probably be as effective.

In analysis of light lanthanon group elements, inasmuch as volatilization characteristics are very similar, there would appear little risk of preferential distillation of an element in the arc. In the heavy group, however, there is a wider range of volatilities (especially so in the case of ytterbium) so that greater care has to be taken in such analysis. Fassel *et al.* (*loc. cit.*) always arc their samples to completion, the endpoint being taken as the development of an unstable arc, sudden drop in arc current, and an increase in the voltage drop across the electrodes.

The general efficiency and sensitivity of arc spectroscopy has tended to obscure the value and ease of operation of spark techniques. Much work was carried out between 1880 and 1910 on lanthanon spark spectra but there is much discrepancy in the line values given, and the purity of materials employed in the early work is of course dubious. More recent work in this field would indicate that spark spectra appear to offer better precision and accuracy than arc spectra because of the more complete energization. However, spark excitation is not so easily adaptable to the analysis of rocks and minerals as is the arc.

Feldman⁽²⁰⁾ has summarized the three main methods of applying spark excitation in which the sample is developed by a residue method, an impregnation method, or a continuous feed technique. Spark residue methods suffer less from preferential volatility effects than do arc methods, but the composition of the radiating vapour as a whole may change in either method as the sample is consumed. This change, and the change in excitation conditions which accompanies it, are of major importance for some combinations of elements. Using copper electrodes, Nachtrieb *et al.*⁽²¹⁾, claimed a high degree of reproducibility for spark techniques, and detected and determined rare earth concentrations of the order of 0.01 to 0.05 ppm. Pesic⁽²²⁾ slightly modified Nachtrieb's procedures, and was able to determine Ce (10^{-6} g), Y and La (2×10^{-7} g). Spark technique analyses were also made by Ishida⁽²³⁾ who used, as electrodes, briquettes prepared from graphite and rare earth oxides in a 1:3 ratio. Whilst probably adequate for the more common rare earths, the formation of such electrodes would be a costly business with the heavier elements. Feldman and Ellenburg⁽⁶⁾ evaporated nitrate solutions of the rare earths (containing palladium as an internal standard) onto carbon rods, and then sparked the system in an argon-oxygen mixture.

Excellent results were obtained with a mean deviation of 1.3 per cent. Serious matrix effects exhibited by cerium and lanthanum were overcome by the addition of zinc salts to the solution together with the palladium.

Impregnation techniques usually leave much to be desired, insofar as not all solutions will speedily penetrate the electrode systems used. Moreover, the possibility may arise of preferential intercalation into the graphite of specific rare earths⁽²⁴⁾ leading thus to inadequate, or incomplete, vaporization of the element in the spark.

Emission lines, obtained in the porous cup technique examined by Feldman (*loc. cit.*), are normally as sharp as those obtained by other spark techniques, and successful analyses were obtained with sensitivity limits of the order of 1 to 10 ppm of rare earths. In the same way that substances having high vapour densities often give broad lines with the ordinary spark, solutions which penetrate the porous cup too quickly also produce lines which are weak and show pressure broadening. This is sometimes the case with hydrochloric acid solutions, but can be eliminated by the addition of some indifferent liquid such as sulphuric acid or glycerol to the solution to increase its viscosity. This particular problem can also be eliminated by use of the rotating electrode.

Similar to spark spectroscopy, Piccardi⁽²⁵⁾ has employed a method of molecular flame spectra for analysis of rare earth fractions. Essentially, a spray of rare earth solution is produced in a gas-oxygen flame and rare earth concentrations of *ca.* 1×10^{-4} can be detected and determined by observation of their line spectra. Flame spectra of the rare earth elements have been examined by other workers as well as by Piccardi. Lanthanum has been the subject of most work, Menis *et al.*⁽²⁶⁾ having been able to detect 0.05 γ La/ml in ketone solution using the emission from the oxide bands at 422, 560 and 743 $m\mu$. Titanium, aluminium, interfere with the determination but can be eliminated by prior separational techniques. De Albinati⁽²⁷⁾ has also examined the determination of lanthanum by flame spectrophotometry whilst Lagerquist and Huldt⁽²⁸⁾ have given the full emission curve obtained with lanthanum chloride solutions. Earlier work on yttrium, ytterbium, and lanthanum flame spectra was carried out by Platinga and Rodden⁽²⁹⁾.

As with spectrophotometric methods, it is difficult to reduce spectrographic methods to mechanical procedures, because this

depends to a large extent upon the instrument employed, its dispersion, amperage applied to the arc, type of photographic film, exposure, etc. Ratios of sample to carbon, internal standard, etc., have also varied from worker to worker. Rodden⁽²⁵⁾ uses a 1:5 ratio of sample oxide to graphite, arcs at 10 amps, and exposes film for 40 seconds; after development the plate is examined visually at the following wavelengths:

<i>Element</i>	<i>Wavelength (Å)</i>	
Ho	3416.46	3398.98
La	3988.52	3265.67
Lu	2911.39	2900.13
Nd	3951.15	3963.11
Pr	4008.71	
Sc	3353.73	3613.84
Tb	3324.40	
Th	2870.41	4019.14
Tm	3131.26	3151.04
Y	3242.28	3200.27 3216.68
Yb	3289.37	

When an internal standard (La) is used, the following impurity lines are determined:

<i>Element</i>	<i>Wavelength (Å)</i>
Dy	3407.80
Gd	3422.47
Eu	3971.99
Er	3264.78
Sm	3634.27
La	3376.33

Fassel (*loc. cit.*), on the other hand, tabulates his procedure as follows:

Spectrograph	Jarrell-Ash 6 m stigmatic grating spectrograph
Upper electrode (cathode)	Graphite rod 3 mm × 25 mm pointed at one end
Lower electrode (anode)	Shallow thin walled graphite electrode (6 mm diam. with 2 mm deep cavity and wall thickness of $\frac{1}{2}$ mm) containing 1:1 mixture of the ignited rare earth oxides and 200 mesh graphite. Anode is supported on 3 mm graphite pedestal.

Analytical gap	4 mm
Excitation source	d.c. arc 250 V 17-18 amp
Length of exposure	Sample arced to complete consumption
Emulsion	Spectrum analysis No. 1 (3000-4300 Å); Kodak M (4000-5000 Å)
Wavelength region	3300-4600 Å second order
Development	4 min at 21° in Eastman Kodak D-19 with agitation
Densitometry	ARL comparator densitometer
Emulsion calibration	Two step sector, preliminary curve method

The spectral lines selected for comparison will vary from worker to worker and according to the nature of the analysis required.

TABLE 7-3. INTERNAL STANDARD LINE PAIRS

Element and line	Standard and line	Concentration range (per cent)	Detection limit (per cent)
Sc 4023.7	Fe 4009.7	0.01-0.5	0.0002
3613.8	3603.2	0.01-0.5	0.0002
3642.8	3603.2	0.01-0.5	0.0002
3613.8	Pt 3204.04	0.01-0.5	0.0002
3353.7	Zr 3357.3		
3199.37	Y 3242.3	0.01-1.0	0.005
3330.6	Tm 3362.6	0.01-1.0	0.005
3613.8	Yb 3655.73	0.01-1.0	0.005
4246.8	Lu 3280.5	0.01-1.0	0.005
Y 3600.7	Fe 3603.2	0.02-1.0	0.0005
3195.6	Al 3060.0	0.001-0.1	0.001
3179.4	Al 3060.0	0.001-0.1	0.001
4309.6	Sr 4215.5	1-100	
4374.9	Ce 4373.8	0.6-57	
3601.9	Dy 3611.9	0.02-1.0	0.007
4374.9	Ho 4379.1	0.01-1.0	0.005
3982.6	3966.9	0.01-1.0	0.008
4374.9	Er 4382.2	0.01-1.0	0.0007
La 4333.7	Fe 4337.0	0.05-1.0	0.0002
3988.5	4009.7	0.05-1.0	0.0002
3995.8	4009.7	0.05-1.0	0.0002
4429.9	Sr 4215.3	1-100	0.0002
4238.4	4215.3	1-100	
4196.6	4215.3	1-100	
3245.12	Al 3060.0	0.001-0.07	0.001
3215.81	3060.0	0.001-0.07	0.001
4269.5	Ce 4264.4	10-60	
3995.8	3995.4	0.04-2.0	0.005
3337.5	Pr 3341.5	0.1-2.0	0.005
Ce 4562.4	Ce 4603.0	0.25-2.0	0.005
4572.3	4603.0	0.25-2.0	0.005
4222.6	Al 3060.0	0.001-0.1	0.001
3256.7	3060.0	0.001-0.1	0.001
4298.9	La 4293.5	0.05-1.0	0.03
4539.8	Pr 4540.5	0.10-2.0	0.08
Pr 4008.7	Fe 4009.7	0.002-0.05	0.002
3908.4	3898.0	0.002-0.05	0.002
4241.0	Al 3060.0	0.101-0.1	0.001
4225.3	3060.0	0.101-0.1	0.001
3245.5	3060.0	0.101-0.1	0.001
4222.98	Sr 4215.5		
4408.8	Ce 4413.8	1-15	
4225.3	4239.0	0.05-2.0	0.02
4408.8	La 4393.5	0.05-1.0	0.03
4408.8	Nd 4419.6	0.2-4.0	0.1

TABLE 7-3—continued

Element and line	Standard and line	Concentration range (per cent)	Detection limit (per cent)
Nd 4061.1	Fe 4009.7	0.1-2.0	0.002
4303.6	4337.0	0.1-2.0	0.002
4247.4	Al 3060.0	0.001-0.1	0.001
3275.2	3060.0	0.001-0.1	0.001
4446.4	Ce 4455.0	5-50	
3973.3	La 3925.1	0.05-1.0	0.02
4061.1	Ce 4093.3	0.02-2.0	0.02
4400.8	Pr 4401.4	0.1-2.0	0.05
Eu 3972.0	Fe 3977.7	0.01-0.5	0.0002
4661.9	4603.0	0.01-0.5	0.0002
3280.7	Al 3060.0	0.001-0.1	0.001
3906.7	3060.0	0.001-0.1	0.001
4435.6	Sr 4215.5	1-100	
3972.0	4215.5	1-100	
4129.7	Sm 4129.2	0.1-2.0	
4627.1	4628.8	0.01-0.3	
Gd 4347.3	Fe 4352.7	0.1-2.0	0.002
3362.2	3369.5	0.1-2.0	0.002
3350.5	3369.5	0.1-2.0	0.002
3358.6	3369.5	0.1-2.0	0.002
3046.5	Al 3060.0	0.001-0.1	0.001
3034.06	3060.0	0.001-0.1	0.001
4251.7	Sr 4215.5	1-100	
4342.2	4215.5	1-100	
4262.1	Ce 4283.6	0-10	
3350.5	Y 3377.7	0.02-2.0	
4327.1	4291.0	0.1-2.0	
Tb 3509.2	Fe 3445.2	0.1-2.0	0.002
3324.4	3369.5	0.1-2.0	0.002
3702.9	Sr 4215.5	1-100	
3703.9	4215.5	1-100	
3874.2	4215.5	1-100	
2218.4	Y 3182.4	0.1-2.0	
4318.0	Dy 4319.2	0.2-2.0	0.1
Dy 4000.45	Fe 4009.7	0.02-2.0	0.0005
4211.7	4233.6	0.02-2.0	0.0005
3531.7	3603.2	0.02-2.0	0.0005
3251.3	Al 3060.0	0.001-0.1	0.001
3232.6	3060.0	0.001-0.1	0.001
3407.8	Y 3393.1	0.01-0.2	
3407.8	3450.95	0.1-2.0	
3944.7	Sr 4215.5	1-100	
4221.1	Ho 4221.6	0.04-1.0	0.04
3898.5	Er 3891.7	0.01-1.0	0.005
Ho 3456.0	Fe 3369.5	0.01-0.5	0.0002
4053.9	4009.7	0.01-0.5	0.0002
3891.0	Sr 4215.5	1-100	
4103.8	4215.5	1-100	
3453.1	Y 3393.1	0.02-0.2	
3456.0	Dy 3443.5	0.02-1.0	0.02
3456.0	Er 3437.0	0.01-1.0	0.005
Er 3499.1	Fe 3445.2	0.5-100	0.0005
3372.8	3369.5	0.5-100	0.0005
3906.3	Sr 4215.0	1-100	0.0005
4008.0	Dy 4005.5	0.02-1.0	0.02
3906.3	Ho 3910.3	0.01-1.0	0.01
Tm 3462.2	Fe 3369.5	0.02-2.0	0.001
3362.6	3369.5	0.02-2.0	0.001
3131.3	3369.5	0.02-2.0	0.001
3761.3	Sr 4215.5	1-100	0.001
3761.9	4215.5	1-100	
3848.0	4215.5	1-100	
3362.6	Er 3328.3	0.01-1.0	0.001

TABLE 7-3— continued

Element and line	Standard and line	Concentration range (per cent)	Detection limit (per cent)
3441.5	Yb 3436.5	0.01-1.0	0.003
3462.2	Lu 3491.9	0.02-1.0	0.002
3362.6	Sc 3330.6	0.01-1.0	0.005
Yb 3464.4	Fe 3445.2	0.02-2.0	0.0002
3289.4	3286.8	0.02-2.0	0.0002
3694.2	Sr 4215.5	1-100	
3988.0	4215.5	1-100	
3261.5	Al 3060.0	0.001-0.1	0.001
3031.1	3060.0	0.001-0.1	0.001
2859.8	3060.0	0.001-0.1	0.001
3987.0	Er 3977.6	0.005-0.2	0.001
2970.6	2986.7	0.001-1.0	0.0001
2970.6	Tm 2961.4	0.02-1.0	0.005
3289.4	Tm 3284.6	0.02-1.0	0.0002
2970.6	Lu 2931.5	0.02-1.0	0.005
3289.4	3280.5	0.008-0.01	0.0005
2970.6	Sc 2913.0	0.01-1.0	0.004
Lu 3359.6	Fe 3369.5	0.01-0.5	0.0002
3312.1	3369.5	0.01-0.5	0.0002
3354.4	Sr 4215.5	1-100	
3472.5	Tm 3459.7	0.02-1.0	0.005
3312.1	3327.2	0.01-1.0	0.005
3281.7	Sc 3240.7	0.01-1.0	0.005

Table 7-3 lists the most valuable spectral comparisons, etc. Because any accurate spectrochemical analysis will be based upon densitometric observation of line intensities, and comparison with those of the standards (internal or external), it is not yet possible to establish a system of coefficients as in spectrophotometric work.

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CHAPTER VIII

X-RAY ABSORPTION AND EMISSION SPECTROMETRY

ALTHOUGH, IN the broad sense, structure determination by X-ray diffraction studies may be construed as analytical in nature, it will not be thus considered in this volume. The literature is replete with standard text books on X-ray diffraction techniques and interpretation of data obtained therefrom but, unless one is dealing with a known system, identification of the atoms producing the crystal structure is, in general, a virtual impossibility. Additionally, X-ray crystal studies will rarely detect the presence of less than 5 per cent of a minor constituent in a matrix, and then only if the parameters of the sought-for crystal material are known, or have been determined by the analytical procedures considered in this and other chapters of this volume. Copeland and Bragg⁽¹⁾ and Clark and Reynolds⁽²⁾ have applied the theory of Alexander and Klug⁽³⁾ to quantitative X-ray analysis of known systems, and future work may present in this a new analytical use of the X-ray tool. Thus far, however, studies are considered insufficiently clarified for immediate adaptation to rare earth analysis.

X-RAY ABSORPTION

In Chapter VI we considered specifically, absorption of visible light by rare earth ions in solution and, although X-ray absorption does not present such dramatic effects, the absorption phenomena can be applied with a certain degree of accuracy, not only to the specific, coloured, rare earth ions, but to all of them. Just as the wavelength of an emission line is characteristic of an element so, to a first approximation is its absorption wavelength. If, therefore, the absorption of a sample containing a number of elements is measured as a function of wavelength, absorption edges will be found which, by their wavelength, serve to identify the various elements in the sample. If the intensity be measured by absorption at each edge,

quantitativeness can be defined with some accuracy. An additional advantage also lies in the fact that, providing that one confines examination to a specific set of absorption edges (e.g. those attributable to *K* level absorption) little or no interference occurs from 'alien' or matrix elements.

Absorption of energy through any region of the electromagnetic spectrum involves transition of electrons in the atomic orbitals from one energy level to another. In absorption in the visible, this transition is at the 4f (*N*) level; in the X-ray region, transitions involving lower, *K*, *L*, *M*, etc., levels can be detected. The absorption of X-ray energy by transitions of this nature in an element does not produce band spectra as in the visible region, but rather discontinuities in the energy absorption slope presented by a matrix. Just as the impact of an electron can expel an electron from an atomic orbital and thus cause the emission of characteristic radiation, so also can an incident quantum of X-rays, provided it possesses the minimum amount of energy. This implies that the wavelength of the imposed X-radiation must be less than a certain value, λ , since the energy per quantum is $h\nu$ and wavelength is proportional to frequency. This relationship may be written: $W = h\nu = hc/\lambda$ where ν and λ are the frequency and wavelength respectively of the absorption discontinuity produced by absorption of energy by electrons at a given orbital level. Thus the absorption edge will be found at increasing wavelength values for the *K*, *L*, *M*, etc., levels respectively. One edge is found for the *K* level; absorption at the *L* level is shown by three, and at the *M* level by five, edges. The measured values of the absorption edges can be used to construct an energy level diagram for the atom which, in turn, can be used for the calculation of characteristic, line emission, wavelengths.

Kramers⁽⁴⁾ first developed a law governing the continuous absorption of X-radiation using the methods of classical electrodynamics based upon the Bohr model of the atom. He found the following formula for the atomic coefficient, i.e. the percentage absorption per atom in a column of 1 cm² cross section at any wavelength, λ , shorter than the wavelength, λ_n , of the *n*th absorption limit of an element of atomic number *Z*:

$$a_v(n) = \frac{64\pi^4 e^{10} m}{3\sqrt{3} c^4 h^6} \frac{Z^4 \lambda^3}{a_n n^3}$$

where the central quotient = 0.0104; g is a factor near unity and $a_n = n(n+1)$ is the statistical weight of the n th state. Such absorption, of course, results in the ejection from the atom of an electron with a certain velocity, v , as given in the photo-electric equation:

$$\frac{1}{2}mv^2 = hc/\lambda - hc/\lambda_n$$

Many similar calculations may also be thus derived from absorption studies, but here we are concerned with those relating, for example, the K absorption curve, and its intensity with an element and its concentration. Specifically, we are concerned with the simple relationship:

$$I = I_0 e^{-(\mu/\rho)m^p m^t}$$

$$\text{or } \ln I_1/I_2 = W_A K_A M_M$$

where W_A = weight fraction of A , $M_M = \rho, m^t$ = density times thickness of the sample, and K_A measures the mass absorption coefficient of A at the absorption edge and is an intrinsic property of the element.

It will be noted that we have been specifically considering the K level edge of absorption. This is generally the most specific and easily found absorption level for an element, although because of power limitations of commercial X-ray tubes it has been suggested⁽⁵⁾ that, when the atomic number of the element being determined exceeds 50, the L_{iii} edge should be examined. This proviso should not be accepted without constraint, however, since it has been shown in, for example, gadolinium carbide⁽⁶⁾ that the L_{iii} edge is grossly erratic and quite different from that of the oxide or the metal. Similarly, it has been variously shown⁽⁷⁾ and particularly with the rare earths⁽⁶⁾ that some modification of the K edge can occur with variation in nature, covalency, or co-ordination of the compound under investigation. The variations, though not so dramatic, may be considered analogous to variations found in the visible absorption spectra of rare earth ions under the influence of complex-forming ions. Wherever possible, therefore, use of high voltage target tubes should be impressed in order to obtain the lowest possible level of absorption.

Application of X-ray absorptiometry to analysis has been examined by several workers, amongst whom Vainshtein⁽⁸⁾ has probably made the most recent and apt studies directly associated with determination

of the rare earth elements. Liebhafsky⁽⁹⁾ has frequently reviewed the literature on the subject, and it would appear that the first direct application of this technique to analysis was effected by Glocker and Frohnmayer in 1925⁽¹⁰⁾. In specific application to rare earth analysis, Vainshtein (*loc. cit.*) has obtained several applicable equations for their determination.

$$A_i = n_i A_o$$

where A_i is the content of the element sought, n_i is a coefficient characterizing the relative composition of the sample, and A_o is the content of the comparison, or standard, element. If the sum of the rare earths is known (S), individual calculation can be made from:

$$A_i = n_i S / \sum_{i=0}^{i=13} n_i$$

When all rare earths are present in the sample, the width of the spectral absorption line is taken as a measure of individual content, and n_i is obtained from the intensity ratio of two lines. When only a few rare earths are present, previously derived functions of the darkening factor are used.

Either Vainshtein's equations, or those immediately derived from the absorption coefficients (above) can be applied with equal accuracy.

Absorption measurements may be made using both polychromatic and monochromatic beams, of X-rays. The absorption of a polychromatic beam, obtained by the appropriate screening out of characteristic radiation from an X-ray tube and using only the continuous radiation, is simply established. The sample is merely placed in the direct beam from the X-ray tube and a counter behind the sample measures the transmitted intensity. Because of the multiplicity of wavelengths present, no exact calculation can be made of transmitted intensity as a function of sample composition. However, a calibration curve can be set up on the basis of samples of known composition and the wavelengths used can be restricted by the use of appropriate filters. The curve obtained will be valid for the determination of a specific element in a series of samples providing that the element sought is the only one whose absorption edge falls within the wavelength region permitted by the filters.

As Cullity⁽⁵⁾ points out, the chief advantage of this method is the

very large gain in intensity over methods involving monochromatic beams which are quite feeble in comparison with the direct beam from an X-ray tube.

Nevertheless, use of monochromatic X-ray beams is more applicable to absorption analysis. Monochromaticity is most generally obtained by diffraction of X-radiation from a single crystal, for example, of lithium fluoride. This is mounted in the centre of the goniometer of the customary diffractometer; filtered $\text{Cu } K\alpha$ radiation, obtained in the usual manner, is impinged on to, and diffracted at specific wavelengths from, the crystal. As the crystal is rotated through 2θ angles, the diffracted wavelength varies and passes through the sample. Absorption is then measured by Geiger or scintillation counter as a function of wavelength (or rather 2θ which is converted directly to λ using the appropriate parameters for the crystal spacing).

TABLE 8-1. ABSORPTION EDGES AND COEFFICIENTS

Element	Absorption edge (X-units)		Mass absorption coefficients μ/ρ						
	K	L_{III}	Ag $K\alpha$ $\lambda 0.5604$	Rh $K\alpha$ 0.6149	Mo $K\alpha$ 0.7097	Cu $K\alpha$ 1.5392	Ni $K\alpha$ 1.6565	Fe $K\alpha$ 1.9344	Cr $K\alpha$ 2.2869
Sc	2751.7		10.5	13.8	21.1	185	222	338	545
Y	725.5	5944.4	55.5	74.0	108.9	129	158	235	360
La	318.14	2253.7	26.0	33.0	47.9	378	444	632	218
Ce	306.26	2159.5	28.4	35.8	52.0	407	476	636	235
Pr	295.1	2072.8	29.4	37.2	54.5	422	493	624	251
Nd	284.58	1990.7	30.5	38.8	57.0	437	510	651	263
Sm	264.4	1840.8	33.1	41.2	62.3	467	519	183	289
Eu	254.8	1771.7	35.0	44.5	65.9	461	498	193	306
Gd	246.2	1706.0	35.8	45.7	68.0	470	509	199	316
Tb	237.6	1645.3	37.5	47.9	71.7	435	140	211	333
Dy	230.1	1576.0	39.1	49.9	75.0	462	146	220	345
Ho	222.64	1532.2	41.3	52.7	79.3	128	153	232	361
Er	214.8	1479.19	42.6	54.6	82.0	139	159	242	370
Tm	208.5	1429.9	44.8	57.6	86.3	144	168	257	387
Yb	201.6	1382.64	46.1	59.4	88.7	151	174	265	396
Lu	195.1	1337.5	48.4	62.6	93.2	157	184	281	414

When the sample is interposed in the monochromatic X-ray beam, the transmitted radiation is measured for a series of wavelengths on either side of the absorption edges of the expected elements. In practice, with automatic recording via Geiger counting, a complete chart, or charts, of absorption can be obtained for the substance under examination from which, by comparison of absorption wavelengths, a qualitative impression can be evinced of the elements present in the sample, and a quantitative evaluation made by use of the appropriate equations above. Table 8-1 lists absorption edges and coefficients for the rare earth elements and Fig. 8-1 the type of curve obtained from a rare earth oxide sample.

It is essential that the absorbing sample be very thin in section and in the case of alloy samples it may be necessary to reduce the thickness to 1–2 thousandths of an inch. When the sample is available in the form of a powder, two techniques would appear permissible. The sample may be pressed (and preferably sintered) into a thin wafer, or, as a powder or paste with, for example, vaseline, pressed into the slot of a filter holder milled down to give a plate of about 0.5 mm thickness. Extreme care must be taken to ensure homogeneity of the sample and adequacy of packing so that voids or localized concentrations do not occur. It would seem that X-ray absorptiometry of solutions would be a preferable technique, but this does not appear to have been investigated.

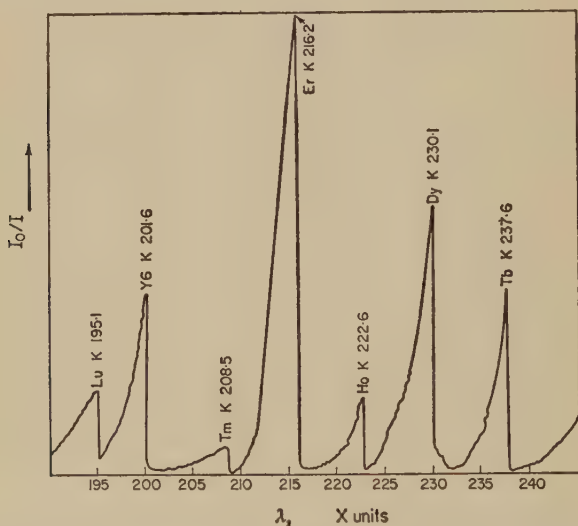


FIG. 8-1. X-ray absorption analytical curve for heavy lanthanon oxide sample.

Barieau⁽¹¹⁾ has increased the sensitivity of X-ray absorption methods by replacing the Geiger counter by a scintillation counter, and electronically discriminating out the harmonics reflected by the lithium fluoride crystal.

For high concentrations, X-ray absorptiometry is to be preferred over X-ray emission spectrometry (see below) because of the lack of matrix, or interference, effect. It is not as sensitive as X-ray emission,

however, but is inherently more accurate than emission spectrography in the visible because of the greater stability of X-ray, as compared to spectrographic, sources. On the other hand, unless recording equipment is applied, each element must be determined separately as compared with the several elements determinable simultaneously with the emission spectrograph.

X-RAY EMISSION

Because of the small number of lines in a characteristic X-ray emission spectrum, and because of the direct relation of intensity of a characteristic line to the amount of an element present in the examined material, emission spectrometry in the X-ray region offers considerable advantages in some respects over spectrochemical analysis in the visible and ultra violet regions. Older work (usually termed X-ray fluorescence analysis) was much restricted by the availability of means for measuring the relatively feeble rays emitted upon radiation of a specimen by X-rays. Instrumental improvements have, however, overcome this difficulty and also the limitations imposed by absorption and diffraction of the emitted spectra by air. High vacuum and helium ray paths, together with high intensity X-ray sources and scintillation counters (instead of Geiger tubes) now permit analyses for elements down to aluminium. Early work suggested that the limit of applicability of X-ray emission spectrography was about 1 per cent concentration of a particular rare earth⁽¹²⁾. This has, in general, been verified although the most recent work of Lytle and Heady⁽¹³⁾ has extended studies into the 0.1–1.0 per cent region with an accuracy of *ca.* 10 per cent. Below about 1 per cent concentration, however, arc emission spectrography may be conceded to be far more accurate; nevertheless, in qualitative terms, X-ray emission spectrography is of increasing importance in rare earth analysis, and particularly so where non-destructive methods are imperative.

The historic method of X-ray spectrography as employed by Moseley⁽¹⁴⁾ is hardly applicable to analysis. The dismountable tube must be evacuated before analysis, specimen form is sometimes difficult to ensure and the heat produced in the sample by electron bombardment may vaporize some contained elements. More effective and applicable is external X-radiation.

Primary radiation is reflected from the sample and the secondary emission diffracted from the lattice planes of known d spacing in a single crystal. Radiation of only a single wavelength is reflected for each angular setting of the crystal and the intensity of this can be measured with a suitable counter. Cullity⁽⁵⁾ has very simply compared X-ray with optical spectrometry which serves to illustrate the main differences:

	<i>Optical</i>	<i>X-ray</i>
exciting agent	arc or spark	X-rays
emitted radiation	visible	X-rays
analyser	prism or grating	crystal
detector	film or phototube	film or counter
nature of spectra	complex	simple

Most X-ray emission spectrometers have the analysing crystal and counter mechanically coupled as in a diffractometer. Thus, when the crystal is set at a particular Bragg angle, the counter is automatically set at the corresponding angle 2θ . The counter is connected to a scaler or to a ratemeter and automatic recording. The intensity of individual spectral lines emitted by the sample may be measured with the counter-scaler combination or the whole spectrum may be continuously scanned and recorded automatically.

Fig. 2 shows an example of the X-ray emission spectrum of a rare earth oxide sample automatically recorded with a G.E. X-ray spectrometer. The wavelength of each line is calculable from the corresponding Bragg angle and the interplanar spacing of the analysing crystal. In the instance demonstrated, the crystal was of lithium fluoride.

In X-ray spectrometry the emission from the sample should be as intense as possible so that it will be adequately and accurately measurable in a short space of time. The best exciting agent, therefore, will be a strong characteristic line of wavelength just shorter than that of the K absorption edge of the emitting elements. It is clearly impossible to meet this requirement for more than one element at a time, and, in practice, a tungsten target tube is used with as high a power rating as possible. The exciting radiation is then that part of the continuous spectrum, and such L lines of the tungsten spectrum, as have shorter wavelengths than the absorption edge of the emitting element.

The useful range of wavelengths extends from about 0.5 to about 2.5 Å, the lower limit being imposed by the maximum voltage which can be applied to the X-ray tube — about 50 kV in commercial

instruments. At this voltage the short wave limit of the continuous spectrum is $0.25 \text{ \AA}$ and maximum intensity occurs at about $0.38 \text{ \AA}$.

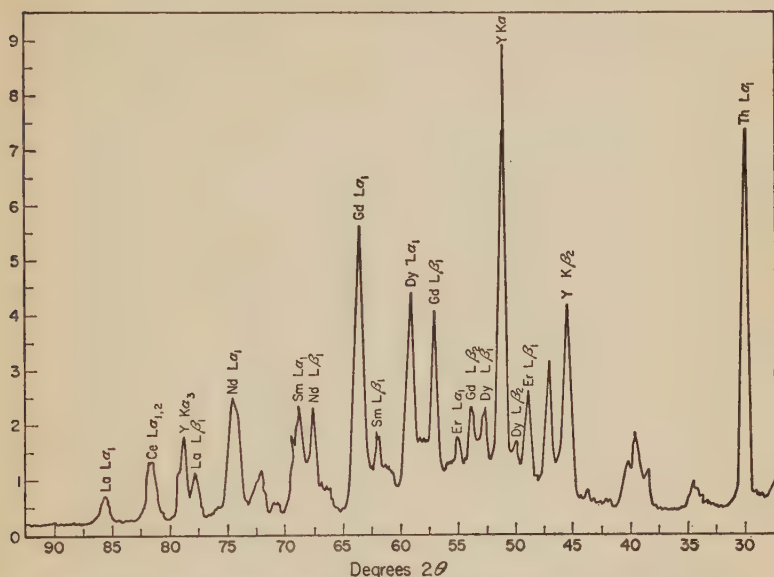


FIG. 8-2. X-ray emission spectrum of heavy oxide mixture. LiF crystal.

In qualitative work sufficient accuracy can be obtained by automatic scanning of the spectrum with the counter output feeding the chart recorder. Interpretation then proceeds through calculation of the line wavelength via the λ and 2θ parameters for the particular analysing crystal, and comparison of the line wavelengths with the principal K and L lines of all the elements arranged in numerical order of wavelength. Complete tables of X-ray emission lines and 2θ values for all analysing crystals in use are not available. Their preparation would be voluminous and, to be complete, would have to include all higher order reflections for all the lines. A substitute is possible, however, consisting of graphs of 2θ vs. λ for each crystal and a numerical tabulation of emission wavelengths. Such data have been presented⁽¹⁵⁾ and it is from these that Table 8-2 has been prepared. It is clearly seen that the X-ray emission lines for the rare earths form three clusters; lines attributable to K level excitation appear between 0.2 – $0.38 \text{ \AA}$, those of the L series more widely spread

between 1.18 and 2.5 Å, whilst the *M* series of lines are thinly dispersed between 6.5 and 14.5 Å.

At a tube voltage of 50 kV little or no *K* emission is produced in elements with atomic numbers higher than 55 and for these analysis is effected via the *L* lines.

TABLE 8-2. X-RAY EMISSION LINES OF THE RARE EARTH ELEMENTS

λ	Element	Series	Line	λ	Element	Series	Line
0.197	Lu	<i>K</i>	β_2	0.256	Gd	<i>K</i>	β_3
0.202	Lu	<i>K</i>	β_1	0.258	Eu	<i>K</i>	β_2
0.203	Yb	<i>K</i>	β_2	0.258	Er	<i>K</i>	α_3
0.203	Lu	<i>K</i>	β_3	0.261	Ho	<i>K</i>	α_1
0.208	Yb	<i>K</i>	β_1	0.264	Eu	<i>K</i>	β_1
0.209	Yb	<i>K</i>	β_3	0.265	Eu	<i>K</i>	β_3
0.215	Tm	<i>K</i>	β_1	0.266	Ho	<i>K</i>	α_2
0.216	Tm	<i>K</i>	β_3	0.267	Sm	<i>K</i>	β_2
0.217	Er	<i>K</i>	β_2	0.270	Dy	<i>K</i>	α_1
0.222	Er	<i>K</i>	β_1	0.274	Sm	<i>K</i>	β_3
0.223	Er	<i>K</i>	β_3	0.274	Sm	<i>K</i>	β_1
0.229	Lu	<i>K</i>	α_1	0.275	Dy	<i>K</i>	α_3
0.231	Dy	<i>K</i>	β_2	0.279	Tb	<i>K</i>	α_1
0.234	Lu	<i>K</i>	α_2	0.284	Tb	<i>K</i>	α_2
0.236	Yb	<i>K</i>	α_1	0.287	Nd	<i>K</i>	β_2
0.237	Dy	<i>K</i>	β_1	0.289	Gd	<i>K</i>	α_1
0.238	Dy	<i>K</i>	β_3	0.294	Gd	<i>K</i>	α_2
0.239	Tb	<i>K</i>	β_2	0.294	Nd	<i>K</i>	β_3
0.241	Yb	<i>K</i>	α_2	0.294	Nd	<i>K</i>	β_1
0.244	Tm	<i>K</i>	α_1	0.297	Pr	<i>K</i>	β_2
0.246	Tb	<i>K</i>	β_1	0.299	Eu	<i>K</i>	α_1
0.246	Tb	<i>K</i>	β_3	0.304	Eu	<i>K</i>	α_2
0.249	Gd	<i>K</i>	β_2	0.305	Pr	<i>K</i>	β_3
0.250	Tm	<i>K</i>	α_2	0.305	Pr	<i>K</i>	β_1
0.253	Er	<i>K</i>	α_1	0.309	Sm	<i>K</i>	α_1
0.255	Gd	<i>K</i>	β_1	0.309	Ce	<i>K</i>	β_2
0.314	Sm	<i>K</i>	α_2	1.222	Lu	<i>L</i>	γ_1
0.316	Ce	<i>K</i>	β_1	1.228	Yb	<i>L</i>	γ_2
0.317	Ce	<i>K</i>	β_3	1.228	Tm	<i>L</i>	γ_4
0.320	La	<i>K</i>	β_2	1.243	Yb	<i>L</i>	γ_6
0.328	La	<i>K</i>	β_1	1.250	Yb	<i>L</i>	γ_8
0.329	La	<i>K</i>	β_3	1.260	Lu	<i>L</i>	γ_5
0.332	Nd	<i>K</i>	α_1	1.268	Tm	<i>L</i>	γ_3
0.337	Nd	<i>K</i>	α_2	1.268	Yb	<i>L</i>	γ_1
0.344	Pr	<i>K</i>	α_1	1.274	Tm	<i>L</i>	γ_2
0.349	Pr	<i>K</i>	α_2	1.276	Er	<i>L</i>	γ_4
0.357	Ce	<i>K</i>	α_1	1.307	Yb	<i>L</i>	γ_5
0.362	Ce	<i>K</i>	α_2	1.315	Er	<i>L</i>	γ_3
0.371	La	<i>K</i>	α_1	1.316	Tm	<i>L</i>	γ_1
0.376	La	<i>K</i>	α_2	1.321	Er	<i>L</i>	γ_2

TABLE 8-2 — continued.

λ	Element	Series	Line	λ	Element	Series	Line
0.727	Y	K	β_4	1.323	Ho	L	γ_4
0.728	Y	K	β_2	1.336	Lu	L	β_9
0.740	Y	K	β_1	1.342	Lu	L	β_5
0.741	Y	K	β_3	1.343	Lu	L	β_{10}
0.829	Y	K	α_1	1.350	Lu	L	β_7
0.831	Y	K	α	1.355	Tm	L	γ_5
0.833	Y	K	α_2	1.364	Er	L	γ_1
1.179	Lu	L	γ_3	1.364	Ho	L	γ_3
1.185	Yb	L	γ_4	1.370	Lu	L	β_2
1.185	Lu	L	γ_2	1.371	Ho	L	γ_2
1.198	Lu	L	γ_6	1.372	Lu	L	β_{15}
1.204	Lu	L	γ_8	1.374	Dy	L	γ_4
1.222	Yb	L	γ_3	1.384	Yb	L	β_9
1.387	Yb	L	β_5	1.505	Tm	L	β_3
1.392	Yb	L	β_{10}	1.514	Er	L	β_2
1.395	Yb	L	β_7	1.515	Tm	L	β_8
1.402	Lu	L	β_3	1.518	Dy	L	γ_5
1.406	Er	L	γ_5	1.529	Gd	L	γ_3
1.416	Yb	L	β_2	1.530	Tb	L	γ_1
1.417	Dy	L	γ_3	1.530	Tm	L	β_1
1.417	Ho	L	γ_1	1.534	Gd	L	γ_2
1.419	Lu	L	β_6	1.544	Eu	L	γ_4
1.423	Dy	L	γ_2	1.544	Tm	L	β_4
1.424	Lu	L	β_1	1.561	Er	L	β_3
1.427	Tb	L	γ_4	1.567	Er	L	β_6
1.441	Lu	L	β_4	1.567	Ho	L	β_2
1.452	Yb	L	β_3	1.577	Tb	L	β_5
1.462	Ho	L	γ_5	1.587	Er	L	β_1
1.463	Tm	L	β_2	1.591	Eu	L	γ_3
1.466	Yb	L	β_6	1.592	Gd	L	γ_1
1.471	Tb	L	γ_3	1.597	Eu	L	γ_2
1.473	Dy	L	γ_1	1.599	Dy	L	β_7
1.476	Yb	L	β_1	1.601	Er	L	β_4
1.477	Tb	L	γ_2	1.603	Sm	L	γ_4
1.478	Lu	L	η	1.619	Ho	L	β_3
1.485	Er	L	β_9	1.619	Lu	L	α_1
1.485	Gd	L	γ_4	1.622	Ho	L	β_6
1.491	Yb	L	β_4	1.623	Dy	L	β_2
1.494	Er	L	β_7	1.630	Lu	L	α_2
1.494	Er	L	β_{10}	1.632	Eu	L	γ_8
1.635	Yb	L	η	1.747	Tb	L	β_3
1.641	Gd	L	γ	1.757	Er	L	η
1.647	Ho	L	β_1	1.776	Lu	L	ϵ
1.655	Sm	L	γ_3	1.777	Tb	L	β_1
1.657	Eu	L	γ_1	1.779	Sm	L	β_5
1.658	Ho	L	β_4	1.785	Tb	L	β_4
1.659	Tb	L	β_7	1.785	Er	L	α_1

TABLE 8-2—continued.

λ	Element	Series	Line	λ	Element	Series	Line
1.659	Sm	<i>L</i>	γ_2	1.788	Eu	<i>L</i>	β_7
1.667	Tb	<i>L</i>	β_{10}	1.792	Eu	<i>L</i>	β_9
1.672	Yb	<i>L</i>	α_1	1.796	Er	<i>L</i>	α_2
1.681	Dy	<i>L</i>	β_6	1.797	Nd	<i>L</i>	γ_3
1.681	Dy	<i>L</i>	β_3	1.800	Eu	<i>L</i>	β_{10}
1.682	Yb	<i>L</i>	α_2	1.801	Nd	<i>L</i>	γ_2
1.682	Tb	<i>L</i>	β_2	1.807	Gd	<i>L</i>	β_6
1.695	Tu	<i>L</i>	η	1.812	Eu	<i>L</i>	β_2
1.708	Eu	<i>L</i>	γ_5	1.815	Gd	<i>L</i>	β_3
1.710	Dy	<i>L</i>	β_1	1.819	Pr	<i>L</i>	γ_4
1.720	Dy	<i>L</i>	β_4	1.826	Ho	<i>L</i>	η
1.723	Gd	<i>L</i>	β_7	1.831	Yb	<i>L</i>	ϵ
1.726	Tm	<i>L</i>	α_1	1.836	Lu	<i>L</i>	λ
1.726	Sm	<i>L</i>	γ_1	1.845	Ho	<i>L</i>	α_1
1.731	Gd	<i>L</i>	β_{10}	1.847	Gd	<i>L</i>	β_1
1.738	Tm	<i>L</i>	α_2	1.853	Gd	<i>L</i>	β_4
1.742	Tb	<i>L</i>	β_6	1.855	Nd	<i>L</i>	γ_6
1.745	Nd	<i>L</i>	γ_4	1.856	Sm	<i>L</i>	β_7
1.746	Gd	<i>L</i>	β_2	1.856	Ho	<i>L</i>	α_2
1.862	Sm	<i>L</i>	β_9	2.000	Sm	<i>L</i>	β_4
1.870	Sm	<i>L</i>	β_{10}	2.009	Nd	<i>L</i>	β_7
1.874	Pr	<i>L</i>	γ_3	2.016	Nd	<i>L</i>	β_9
1.875	Eu	<i>L</i>	β_6	2.019	Er	<i>L</i>	λ
1.878	Nd	<i>L</i>	γ_1	2.020	Pr	<i>L</i>	γ_5
1.879	Pr	<i>L</i>	γ_2	2.023	Nd	<i>L</i>	β_{10}
1.882	Sm	<i>L</i>	β_2	2.035	Nd	<i>L</i>	β_2
1.887	Eu	<i>L</i>	β_3	2.041	La	<i>L</i>	γ_3
1.894	Yb	<i>L</i>	λ	2.046	Gd	<i>L</i>	α_1
1.898	Dy	<i>L</i>	η	2.046	La	<i>L</i>	γ_2
1.899	Ce	<i>L</i>	γ_4	2.048	Ce	<i>L</i>	γ_1
1.909	Dy	<i>L</i>	α_1	2.049	Gd	<i>L</i>	η
1.920	Eu	<i>L</i>	β_1	2.057	Gd	<i>L</i>	α_2
1.920	Dy	<i>L</i>	α_2	2.086	Ho	<i>L</i>	λ
1.926	Eu	<i>L</i>	β_4	2.091	Pr	<i>L</i>	β_7
1.935	Nd	<i>L</i>	γ_5	2.100	Pr	<i>L</i>	β_9
1.936	Pr	<i>L</i>	γ_8	2.103	Nd	<i>L</i>	β_6
1.946	Sm	<i>L</i>	β_6	2.107	Pr	<i>L</i>	β_{10}
1.955	Tm	<i>L</i>	λ	2.110	Ce	<i>L</i>	γ_5
1.955	Ce	<i>L</i>	γ_3	2.119	Pr	<i>L</i>	β_2
1.960	Ce	<i>L</i>	γ_2	2.120	Er	<i>L</i>	α_1
1.961	Pr	<i>L</i>	γ_1	2.126	Nd	<i>L</i>	β_3
1.962	Sm	<i>L</i>	β_3	2.131	Eu	<i>L</i>	α_2
1.976	Tb	<i>L</i>	α_1	2.141	La	<i>L</i>	γ_1
1.983	La	<i>L</i>	γ_4	2.158	Dy	<i>L</i>	λ
1.986	Tb	<i>L</i>	α_2	2.166	Nd	<i>L</i>	β_4
1.998	Sm	<i>L</i>	β_1	2.166	Nd	<i>L</i>	β_1
2.180	Ce	<i>L</i>	β_7	2.410	La	<i>L</i>	β_3

TABLE 8-2 — continued.

λ	Element	Series	Line	λ	Element	Series	Line
2-188	Ce	<i>L</i>	β_9	2-449	La	<i>L</i>	β_4
2-190	Pr	<i>L</i>	β_6	2-458	La	<i>L</i>	β_1
2-195	Ce	<i>L</i>	β_{10}	2-463	Pr	<i>L</i>	a_1
2-199	Sm	<i>L</i>	a_1	2-473	Pr	<i>L</i>	a_2
2-205	La	<i>L</i>	γ_5	2-482	Sm	<i>L</i>	λ
2-208	Ce	<i>L</i>	β_2	2-512	Pr	<i>L</i>	η
2-210	Sm	<i>L</i>	a_2	2-561	Ce	<i>L</i>	a_1
2-216	Pr	<i>L</i>	β_3	2-570	Ce	<i>L</i>	a_2
2-218	Sm	<i>L</i>	η	2-620	Ce	<i>L</i>	η
2-234	Tb	<i>L</i>	λ	2-665	La	<i>L</i>	a_1
2-255	Pr	<i>L</i>	β_4	2-674	La	<i>L</i>	a_2
2-259	Pr	<i>L</i>	β_1	2-675	Nd	<i>L</i>	λ
2-275	La	<i>L</i>	β_7	2-740	La	<i>L</i>	η
2-282	La	<i>L</i>	β_9	2-764	Sc	<i>K</i>	β_5
2-282	Ce	<i>L</i>	β_6	2-780	Sc	<i>K</i>	β_1
2-290	La	<i>L</i>	β_{10}	2-784	Pr	<i>L</i>	λ
2-303	La	<i>L</i>	β_2	2-892	Ce	<i>L</i>	λ
2-311	Ce	<i>L</i>	β_3	3-031	Sc	<i>K</i>	a_1
2-312	Gd	<i>L</i>	λ	3-032	Sc	<i>K</i>	a
2-349	Ce	<i>L</i>	β_4	3-034	Sc	<i>K</i>	a_2
2-356	Ce	<i>L</i>	β_1	5-283	Y	<i>L</i>	$\gamma_{2,3}$
2-370	Nd	<i>L</i>	a_1	5-875	Y	<i>L</i>	γ_5
2-379	La	<i>L</i>	β_6	5-983	Y	<i>L</i>	β_3
2-382	Nd	<i>L</i>	a_2	6-018	Y	<i>L</i>	β_4
2-395	Eu	<i>L</i>	λ	6-094	Y	<i>L</i>	β_6
2-409	Nd	<i>L</i>	η	6-211	Y	<i>L</i>	β_1
6-449	Y	<i>L</i>	a_1	9-213	Ho	<i>M</i>	$a_{1,2}$
6-456	Y	<i>L</i>	a_2	9-228	Ho	<i>M</i>	$a_{1,2}$
6-761	Lu	<i>M</i>	γ	9-364	Dy	<i>M</i>	β
7-023	Yb	<i>M</i>	γ	9-543	Dy	<i>M</i>	$a_{1,2}$
7-040	Y	<i>L</i>	η	9-574	Dy	<i>M</i>	$a_{1,2}$
7-356	Y	<i>L</i>	λ	9-593	Dy	<i>M</i>	$a_{1,2}$
7-545	Er	<i>M</i>	γ	9-599	Sm	<i>M</i>	γ
7-600	Lu	<i>M</i>	β	9-606	Dy	<i>M</i>	$a_{1,2}$
7-840	Lu	<i>M</i>	a_1	9-627	Dy	<i>M</i>	$a_{1,2}$
7-865	Ho	<i>M</i>	γ	9-639	Dy	<i>M</i>	$a_{1,2}$
7-909	Yb	<i>M</i>	β	9-792	Tb	<i>M</i>	β
8-139	Yb	<i>M</i>	a_1	9-937	Tb	<i>M</i>	$a_{1,2}$
8-144	Dy	<i>M</i>	γ	9-966	Tb	<i>M</i>	$a_{1,2}$
8-155	Yb	<i>M</i>	a_2	10-009	Tb	<i>M</i>	$a_{1,2}$
8-246	Tm	<i>M</i>	β	10-023	Tb	<i>M</i>	$a_{1,2}$
8-460	Tm	<i>M</i>	$a_{1,2}$	10-253	Gd	<i>M</i>	β
8-485	Tb	<i>M</i>	γ	10-415	Gd	<i>M</i>	$a_{1,2}$
8-593	Er	<i>M</i>	β	10-449	Gd	<i>M</i>	$a_{1,2}$
8-801	Er	<i>M</i>	$a_{1,2}$	10-504	Nd	<i>M</i>	γ
8-812	Er	<i>M</i>	$a_{1,2}$	10-744	Eu	<i>M</i>	β
8-828	Er	<i>M</i>	$a_{1,2}$	10-954	Eu	<i>M</i>	$a_{1,2}$

TABLE 8-2 — continued.

λ	Element	Series	Line	λ	Element	Series	Line
8.844	Gd	<i>M</i>	γ	10.997	Pr	<i>M</i>	γ
8.850	Er	<i>M</i>	$\alpha_{1,2}$	11.025	Eu	<i>M</i>	$\alpha_{1,2}$
8.965	Ho	<i>M</i>	β	11.260	Sm	<i>M</i>	β
9.161	Ho	<i>M</i>	$\alpha_{1,2}$	11.277	Sm	<i>M</i>	β
9.183	Ho	<i>M</i>	$\alpha_{1,2}$	11.294	Sm	<i>M</i>	β
9.210	Eu	<i>M</i>	γ	11.429	Sm	<i>M</i>	$\alpha_{1,2}$
11.534	Ce	<i>M</i>	γ				
12.064	La	<i>M</i>	γ				
12.400	Nd	<i>M</i>	β				
12.466	Nd	<i>M</i>	β				
12.675	Nd	<i>M</i>	$\alpha_{1,2}$				
13.783	Ce	<i>M</i>	β				
14.058	Ce	<i>M</i>	$\alpha_{1,2}$				
14.510	La	<i>M</i>	β				
14.880	La	<i>M</i>	$\alpha_{1,2}$				
31.072	Sc	<i>L</i>	β_1				
31.393	Sc	<i>L</i>	α				
35.200	Sc	<i>L</i>	η				
35.671	Sc	<i>L</i>	λ				

In quantitative analysis the single line intensity comparison method is used; the intensity I_μ of a particular characteristic line of *A* from an unknown is compared with the intensity I_s of the same line from a standard, normally pure *A* or an added, internal standard. The variation of I_μ/I_s with the concentration of *A* depends markedly upon the other elements present and cannot be predicted by calculation. It is necessary, therefore, to establish the variation by means of measurements made upon samples of known composition.

Where conservative systems are used, such as binary or ternary mixtures, analyses may be simplified by use of non-dispersive techniques. No analysing crystal is employed and the counter receives emitted radiation direct from the sample. Three methods may be employed — selective radiation, selective filtration, or selective counting.

The first of these is accomplished simply by control of the X-ray tube voltage. This is adjusted so that a particular *L* α level is excited and the radiation entering the counter consists almost entirely of the *L* α radiation of the particular element concerned. Since, however, the rare earth excitation levels are very close, high precision is

necessary in adjusting the tube voltage if this technique is to be applied. More specifically, this selective procedure would be applicable in contaminant determination, i.e. Ce in Th, La in U, or Y in Gd or Sc.

Similar considerations oppose both the filtration and selective counting techniques. In the latter instance, however, providing the elements involved differ in atomic number by more than three, adequate analyses can be made by means of a proportional counter and a single channel pulse height analyzer.

The main advantage of non-dispersive methods of analysis is the very large gain in intensity over dispersive methods. The high intensity loss involved in diffraction of the beam from an analysing crystal is completely avoided. The greater the intensity, the shorter the counting time required to obtain a given accuracy, or the higher the accuracy for a given counting time.

Most recent studies of X-ray emission spectrography would seem to have been undertaken by Clark *et al.*⁽¹⁶⁾, Salmon and Blackledge⁽¹⁷⁾, Vainshtein and Turanskaya⁽¹⁸⁾, Dunn⁽¹⁹⁾, Lytle *et al.*^(13, 20), and Fassel and Heidel⁽²¹⁾.

Clark *et al.*, and Salmon and Blackledge, whilst determining the applicability of X-ray spectrography to rare earth analyses, did not investigate the problem far enough to determine the accuracy obtainable by this technique.

Vainshtein and Turanskaya, using barium as an internal standard, followed standard spectrographic procedures; they compared the degree of photographic darkening of two close lines. Cerium, neodymium, praseodymium and lanthanum were thus determined in mixtures with an error of less than 4 per cent.

Dunn studied specifically the *L* line excitation spectra which had been defined by Cauchois and Hulubei⁽²²⁾, and employed chromium as the internal standard. Samples were prepared as pressed buttons and diffraction of emitted radiation was from a mica crystal. Working calibration curves of $\log RE/I_{RE} : I_{Cr}$ were found to be reasonably accurate but matrix effects and line interferences were in general somewhat high.

As in arc emission spectrography, considerable judgment has sometimes to be exercised in selection of the most appropriate X-ray emission lines for analytical purposes. Essentially, of course, the line preferred is one which is of high intensity and subject to but little,

if any, interferences from other elements in the matrix. In their earlier work, Lytle *et al.* found only yttrium, lanthanum, cerium, praseodymium, neodymium and samarium to meet both these criteria. Other rare earths demonstrated at least one interference. Using the L spectra, an interesting observation was made regarding the relative intensities of the rare earth lines. From lanthanum to samarium, the $L\beta_1$ line is more intense than the $L\alpha_1$, at the europium and gadolinium levels the intensities of the lines are approximately the same, but for succeeding elements the intensity ratio inverts until, for lutetium $L\alpha_1 : L\beta_1 :: 2 : 1$. This variation was attributed to the use of an air ray path since, when a helium atmosphere is used throughout the $L\alpha_1$ line is always the more intense. In later work the helium path was used almost exclusively at long wavelengths, although since background and peak intensities were increased by the same factor, no

TABLE 8-3. ANALYTICAL LINES FOR X-RAY EMISSION SPECTROMETRY OF THE RARE EARTHS
(LiF crystal)

Element	Spectral line	Order	2θ angle Lithium fluoride crystal	Possible interferences (rare earths)
Y	$K\alpha$	1	23.82	None
La	$L\alpha_1$	1	82.86	None
Ce	$L\alpha_1$	1	78.97	None
Pr	$L\beta_1$	1	68.23	Th $L\beta^{-3}$
Nd	$L\beta_1$	1	65.07	Dy $L\beta$
Sm	$L\beta_1$	1	59.48	None
Eu	$L\beta_1$	1	56.94	Dy $L\alpha_1$, Th $L\alpha_1^{-2}$
	$L\beta_1$	2	144.88	None
Gd	$L\beta_1$	1	54.56	Ho $L\alpha_1$
	$L\alpha_1$	1	61.06	Nd $L\beta_2$, Ce $L\gamma_1$
Tb	$L\beta_1$	2	123.86	Er $L\alpha_1$
Dy	$L\beta_1$	2	116.23	None
Ho	$L\beta_1$	2	109.64	Eu $L\gamma_1^{-2}$
Er	$L\beta_2$	1	44.16	Th $L\beta_3^{-2}$, Tm $L\beta_3$, Yb $L\beta_4$, Tm $L\beta_1$, Tb $L\gamma_1$
	$L\alpha_1$	1	46.42	Th $L\beta_2^{-2}$, Gd $L\gamma_1$, Lu $L\alpha_1$, Ho $L\beta_2$
Tm	$L\gamma_1$	1	38.14	Th $L\gamma_1^{-2}$
	$L\beta_1$	2	98.88	Tb $L\gamma_1^{-2}$
Yb	$L\beta_1$	1	42.26	Lu $L\beta_4$, Tm $L\beta_4$, Dy $L\gamma_1$
	$L\alpha_1$	2	112.17	Y $K\alpha^{-4}$, Dy $L\beta_1$
Lu	$L\gamma_1$	1	35.32	None
	$L\beta_1$	2	90	Ho $L\gamma_1^{-2}$, Yb $L\beta_2^{-2}$, Th $L\alpha_1^{-3}$

significant increase in sensitivity or accuracy was noted. Using a tungsten target tube, a lithium fluoride diffracting crystal and argon filled proportional counter, analytical spectral lines employed, and interferences found, were those shown in Table 8-3. Particular emphasis was placed by Lytle *et al.* (*loc. cit.*) upon instrument calibration and, after any change in the crystal, Soller slit, tube or counter tube, recalibration is necessary using a standard series of rare earth elements. Background intensity should be determined carefully near, and on both sides of, the analytical line. Earlier work in the upper concentration levels demonstrated an average error of about 3 per cent in the 5 to 100 per cent range and 7 per cent in the 0.2 to 5 per cent range. This latter error would appear to have been somewhat fortuitous since, in their later work, this group found a

TABLE 8-4. APPARATUS AND OPERATING CONDITIONS FOR DETERMINATION OF YTTRIUM

X-ray power supply	Full wave rectified
X-ray tube	Scaled-off type, molybdenum target
Source operation	48 kV peak at 45 mA.
Spectrometer	X-ray spectrograph attachment and diffractometer converted for X-ray fluorescence
Sample	10 ml of solution in Teflon liquid sample holder
Collimation	Precollimation: 16:1; detector collimator: 800:1
Analysing crystal	Topaz, $2d$ spacing = $2.712 \text{ \AA}$.
Goniometer settings (nominal), 2θ degrees	Background 34.63° Y $K\alpha$ ($0.831 \text{ \AA}$) 35.66° Background 36.69° Sr $K\alpha$ ($0.877 \text{ \AA}$) 37.72° Background 38.75°
Detector	Scintillator counter attachment with linear pulse amplifier
Photomultiplier voltage	900 V, with discriminator setting of 5 V
Scaler system	11-stage binary scaler to scale 2048, resolving time $0.5 \mu\text{sec}$
Av. counting rates, c/s	Background 500-650 Y $K\alpha$ 14,000 max. Sr $K\alpha$ 7,500
Total counts	Backgrounds 51,200 (scale 256) Y $K\alpha$ 51,200-409, 600 (scale 256-2048) Sr $K\alpha$ 409,600 (scale 2049)

10 per cent average error between 0.1–1.0 per cent concentrations although individual sensitivities around 0.01 per cent oxide were obtained.

Sample preparation is of high importance and Lytle *et al.* (*loc. cit.*) very carefully ground their samples under alcohol with quartz sand and lithium carbonate before packing the weighed sample into a special Lucite holder. Heidel and Fassel, however, employed samples in solutions as preferable over solid specimens. This permits the convenient addition of the internal standard (Sr) and avoids errors attributable to variations in particle size, surface condition, etc. When samples are examined in relatively dilute solution, the solvent constitutes the major proportion of the matrix and any matrix effects resulting from variations in the rare earth mixture composition tend to become negligible.

The apparatus and operating conditions used by Heidel and Fassel in determination of yttrium are shown in Table 8-4. It will be noted that a topaz crystal was employed and a scintillation counter replaced the usual Geiger tube. Scintillation counting has a higher and more uniform efficiency than the Geiger tube, and does not depart from linearity of response until the count rate exceeds 20,000 counts per second. With the procedure indicated results were obtained which were within 2.8 per cent of those obtained by arc-emission spectrography.

In general, it would appear therefore that, whilst, with some attention to minute detail, analyses for rare earths by X-ray emission spectrography can be effected with some accuracy down to about 1 per cent concentration, determinations of levels below this is best left for arc spectrography unless the X-ray technique is intended for specification types of analysis only on simple binary or ternary systems.

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CHAPTER IX

RADIOCHEMICAL TECHNIQUES

THE APPLICATION of radiochemical techniques to analyses, whilst increasingly appreciated, still remains a highly specialized amalgamation of procedures. We can therefore give here only generalized direction to such applications in analyses for the rare earth elements; more specialized works⁽¹⁾ must be consulted for specific applications. In general, two modes of application only can be considered in the current context, neutron activation, and tracer techniques.

NEUTRON ACTIVATION

Activation analysis involves exposure of samples to deuteron bombardment in a cyclotron, to neutrons generated in a nuclear reactor or, more conveniently, to neutrons emanating from a Ra-Be source. Because the cross sections for neutron activation reactions may vary with the energy of the source, it is important that analytical data be obtained from a source emitting at one definite energy level. It is customary, therefore, for most neutron activation analyses to be carried out using thermal neutron fluxes. If standard samples are irradiated along with the unknown sample, a quantitative analysis may be obtained by comparison of the isotope production ratios. The procedure is unusually free from interferences from other elements because of the unique decay periods of their artificial isotopes and of the radiations which they emit. Nevertheless in some instances, after radioactivation, those elements which do interfere may require removal by chemical separation, for example by ion exchange, or their effect negated by suitable radiometric techniques. Depending upon the nature of the element studied, quantities as low as 10^{-6} to 10^{-11} g have been determined in this manner⁽²⁾. In a number of cases, radioactivation analysis makes it possible to determine the content of elements of high activation cross section by direct measurement of the activity of the irradiated sample. This may be done provided the half life, or radiation energy, of the radioactive isotope

of the element being determined differs sharply from the corresponding values for the radioactive isotopes of the other elements present in the sample. The activation cross sections of these elements must be considerably lower than the element(s) determined.

The applicability of this mode of activation analysis is, however, limited and therefore, in most cases, particularly when determining trace impurities, it is necessary to resort to the chemical separation of the element being determined. This renders possible the simultaneous determination of a large number of elements in the sample.

The method of radioactivation analysis, now contributed to by many workers, was first employed by Hevesy and Levi⁽³⁾, Seaborg and Livingwood⁽⁴⁾ and Grinberg⁽⁵⁾. It would seem significant perhaps, that the first example of activation analysis made use of the relatively strong activities produced in dysprosium and europium under slow neutron capture (a 300 mc Ra-Be source was used). Determination of the intensity of the distinctive 2.4 hr period of Dy¹⁶⁵ produced by irradiation of a yttrium-dysprosium mixture permitted the estimation of as little as 0.1 per cent dysprosium. Similarly, 1 per cent europium was determined in gadolinium by developing the Eu¹⁵² isotope with a half-life of 9 hr. Again, the presence of as little as 10 ppm of thulium in 'spectroscopically pure' erbium oxide has been demonstrated after neutron irradiation⁽⁶⁾. The avoidance in such rare earth analyses of the traditionally difficult separations makes such data of especial interest.

In principle, the sample to be analysed is placed in a homogeneous radiation flux for a length of time sufficient to produce a measurable amount of radioisotope of the element to be determined. The rate of growth of the number of radioactive atoms, N^* , with time, is then given by

$$dN^*/dt = f\sigma_{ac}N - N\lambda N^*$$

which, on integration, yields

$$N^* = \frac{f\sigma_{ac}N}{\lambda}(1 - e^{-\lambda t})$$

where f is the flux in units/cm²/sec

σ_{ac} is the isotopic cross-section for the reaction

N is the number of target atoms

λ is the radioactive decay constant which is connected with half-life by $\lambda = 0.693/T_{1/2}$.

The amount of activity, A_t , in disintegration units per second is given by

$$A_t = \lambda N^* = f\sigma_{ac}N(1 - e^{-\lambda t}) = A\alpha(1 - e^{-0.693t/T_{1/2}})$$

The derivation and explication of these formulae has already been adequately shown by several workers⁽⁷⁾ and need not be iterated here. In fine, the basic equation applicable to activation analysis may be written⁽⁸⁾: Grams of element of natural isotopic composition:

$$\frac{A_t \times M}{6.02 \times 10^{23} \times f\sigma_{ac}} (1 - e^{-0.693/T_{1/2}}) \theta$$

where M is the chemical atomic weight of the element sought, and θ is the fractional abundance of the target isotope in the naturally occurring element. $(1 - e^{-0.693/T_{1/2}})$ is the saturation factor which depends upon the ratio between length of bombardment and the half-life of the isotope formed. Table 9-1 summarizes isotopic cross sections data for the rare earth elements.

According to this equation it is necessary, when attempting to detect a very small mass of the required element, that the flux and activation cross section be large, that the radionuclide formed

TABLE 9-1. CROSS SECTIONS FOR THERMAL NEUTRON CAPTURE

Element	Activation* cross section	Activity formed	$T_{1/2}$
Sc	22	Sc ⁴⁶	85d
Y	1.2	Y ⁹⁰	61h
La	8	La ¹⁴⁰	40h
Ce	0.12	Ce ¹⁴³	33h
Pr	13	Pr ¹⁴²	19.3h
Nd	0.17	Nd ¹⁴⁴	1.8h
Sm	53	Sm ¹⁵³	47h
Eu	678	Eu ¹⁵²	9.4h
Gd	0.9	Gd ¹⁵⁹	18h
Tb	22	Tb ¹⁶⁰	73.5d
Dy	716	Dy ¹⁶⁵	2.5h
Ho	49	Ho ¹⁶⁶	27.3h
Er	1.0	Er ¹⁷¹	7.5h
Tm	100	Tm ¹⁷⁰	127d
Yb	14.8	Yb ¹⁷⁵	4.1d
Lu	19.5	Lu ¹⁷⁶	3.4h

* $\sigma_{ac} \times 10^{24}$ sq. cm per atom for 0.025 eV neutrons.

possess a short half-life and that the element be of low atomic weight and contain the target isotope in relatively high abundance. As a rough guide it is desirable that the generated radioactivity exhibit a half-life between 3 min and 100 hr.

The total amount of activity produced in a sample is also directly proportional to the sample thickness, but this thickness is limited by the self-absorption of the radiation in the sample. Some maximum sample thickness must be designated for each radioisotope counted and this must be chosen such that the accuracy and sensitivity of the activation method are optimal.

Clearly, determination of the net counting yield depends upon information concerning the decay system for the radionuclide measured and in many instances this is particularly difficult to assemble. Calculation of growth of decay products from radioactive materials is a fairly simple matter when the decay chain is limited to two or three members. With longer chains, however, Bateman's equation⁽⁹⁾ is customarily used, but mechanical errors in calculation, difficult to detect, are not uncommon and Flanagan and Senftle⁽¹⁰⁾ and Kirby⁽¹¹⁾ and Kirby and Kremer⁽¹²⁾ have produced a simplified procedure for computing the growth of radioactive decay products. In many instances, however, reference to such data may be unnecessary and good accuracy may be obtained by comparative procedures using samples of known composition. If a number of samples containing varying amounts of an unknown can be dealt with on a routine basis, a calibration curve may be constructed using a series of internal standards.

Boyd⁽⁸⁾ characterizes the comparative method of activation analysis as follows:

'Irradiate a sample of the substance to be analysed together with a standard sample containing a known weight of the element to be determined. Dissolve the samples and add to the solutions a known weight of the element to be determined. Chemically process the added element so as to free it from bulk constituents in the sample and to remove quantitatively any contaminating radioactivities produced in other elements present in the sample. Determine the chemical yield of the procedure. Compare the activity of the unknown with that of the standard sample. As a check on the radiochemical purity of the assay samples, it may be necessary to measure their half lives and to characterize their radiations by means of aluminium or lead absorption curves or otherwise.'

Radioactivity is usually determined in solid samples and, for this reason, the chemical yield is most often determined gravimetrically by weighing the final sample before and after counting. For most samples which are counted as solids, determination of chemical yield with an accuracy of 2 per cent is sufficient since this is the general limit of the counting accuracy. If the yield is to be determined gravimetrically, the mounted sample must be pure and of known composition. If volumetric or colorimetric determination of the chemical yield is used, only those elements which would constitute interferences need be removed.

The effect of physical form of the mounted sample upon counting rate has been very closely studied, and it has been found that the scattering effect in solid samples is subject to high variation, a count obtained on a precipitate being more accurate and reproducible than a count obtained on a solid sample obtained by evaporation. However, flocculent precipitates which are highly hydrated tend to give unsatisfactory deposits because on drying they tend to contract into a number of isolated dense particles which give high, and variable, self absorption and readily tend to flake off.

TABLE 9-2. NEUTRON SOURCES AND AVAILABLE FLUX*

Source	Flux (n sq. cm/sec)
Reactor	10^{10} – 10^{12}
Cyclotron	10^8 – 10^{10}
Van de Graaff	10^5 – 10^6
1 g Ra-Be	10^4 – 10^5
1 curie Sb-Be	10^3 – 10^4
25 mg Ra-Be	10^2 (thermal)

* After Taylor, T. I. and Havens, W. W.: *Nucleonics*, 6, 54, 1950

Activation analysis is not confined to the availability of large, Government-owned, sources or radiation flux. As Meinke and Anderson⁽¹³⁾ have pointed out, while small sources do not give such a profusion of reaction products, they are useful in analysing for certain high yield reactions. Table 9-2⁽¹⁴⁾ lists the flux available from various neutron sources. Although Meinke and Anderson earlier considered that, of the rare earths, only dysprosium could be analysed using low level neutron sources, later work suggested that a number of other rare earths presented activation parameters favour-

able for activation analysis and comparisons were made between the value of activation analysis and that of other techniques⁽⁸⁾ (Table 9-3). In summary, when only a 25 mg Ra-Be source is available, samarium is best determined spectrophotometrically. In mixtures however of, for example, Sm and Eu, Dy and Ho, adequate and accurate determination can be made by joint spectrophotometric and activation techniques. Where high flux sources are available, however, complete reversion to activation analysis is possible.

TABLE 9-3. SENSITIVITY COMPARISON OF ACTIVATION ANALYSIS WITH ALTERNATE TECHNIQUES*
($\mu\text{g/ml}$)

Element	Oak Ridge Reactors		Cu spark	Graphite arc (d.c.)	Flame photometry	Colour reaction
	X-10 $5 \times 10^{11} \text{ n/cm}^2$	LITR 10^{13} n/cm^2				
Sc	0.002	0.0001	0.005	0.0002		0.25
Y	0.01	0.0005	0.01	0.0005	50	
La	0.002	0.0001	0.05	0.0002	5	
Ce	0.1	0.005	0.5	0.005	20	
Pr	0.002	0.0001	0.2	0.002	100	
Nd	0.1	0.005	0.2	0.002	50	
Sm	0.0006	0.00003	0.2	0.002	100	
Eu	0.00003	0.0000015	0.02	0.0002		
Gd	0.02	0.001	0.1	0.002	10	
Tb	0.004	0.0002		0.002		
Dy	0.00003	0.0000015	0.5	0.002	10	
Ho	0.0004	0.00002	0.2	0.005		
Er	0.02	0.001	0.5	0.0005		
Tm	0.002	0.0001	0.05	0.001		
Yb	0.002	0.0001	0.1	0.001		
Lu	0.0003	0.000015	2.0	0.005		

* After Meinke, W. W.: Science, 121, 177, 1955.

Smales⁽¹⁵⁾ has listed the sensitivity of analyses for the rare earth elements by neutron radiation analysis under ideal conditions in the Harwell pile:

Eu, Dy	10^{-12} g
Ho, Lu, Sm	$10^{-11} - 10^{-10} \text{ g}$
La, Sc, Pr, Tb, Tm, Yb	$10^{-10} - 10^{-9} \text{ g}$
Er, Gd, Y	$10^{-9} - 10^{-8} \text{ g}$
Ce, Nd	$10^{-8} - 10^{-7} \text{ g}$

Like analytical methods in general, radioassays are subject to considerable variation in precision and their accuracy has never equalled that of the best analytical methods, but is comparable to that of many in general use.

Instrumental errors and uncertainties can generally be reduced to about 1 per cent and in some cases to about 0.1 per cent by application of properly determined corrections. Sensitivity of Geiger counters to better than 1 per cent is difficult when β activity is being measured but even so sample errors are generally larger than instrumental.

TRACER TECHNIQUES

Since the beginning of the atomic era, the use of radioactive isotope species for 'tracing' of elements, or for studies on their reactions, has increased to the point at which there would appear to be no laboratory unfamiliar with the techniques involved. Since the use of radioactivity in analytical chemistry is intrinsically instrumental, there exists a tendency to accept tracer techniques simply upon the basis of their physical manifestations with little regard for the chemistry of specific species.

Because of the difficult analytical chemistry of the rare earths, tracer techniques are singularly applicable in these studies. Particularly are they of value in, for example, ion exchange studies, where it is required to follow the passage of a rare earth ion through the resin columns. This can be done, not only for one element but several and, although direct monitoring will give a qualitative indication of *where* the radioisotopes are located, determination of particular radiation characteristics will indicate *what* elements are where. Table 9-4 lists the radioactive isotopes of the rare earth series which are useful for analytical purposes.

It is not considered pertinent here to refer to the mechanisms of radioactive decay, units of radiation, dosage, etc. These are more properly and more adequately dealt with in the classical texts (*vide supra*). Similarly, the operation of instruments for the detection and determination of radioactivity are considered to be appreciated and understood before the analyst commences to use radioactive materials.

Studies and analyses employing the dangerous Ce^{144} , Pm^{147} , Y^{90} and Y^{91} isotopes should be undertaken with care, or not at all, unless

highly adequate facilities and trained personnel are available. If possible less dangerous isotopes should be employed.

TABLE 9-4. SELECTED ISOTOPE SPECIES FOR ANALYTICAL USE

Isotope	$T_{\frac{1}{2}}$	Decay and energy
Sc ⁴⁶	85d	β -1.49 γ 1.12
Y ⁸⁸	104d	β 0.8 γ 2.76
Y ⁹¹	57d	β -1.53
La ¹⁴⁰	40h	β -2.12 γ 1.64
Ce ¹³⁹	140d	α , γ 0.8
Ce ¹⁴¹	30d	β 0.55 γ 0.21
Ce ¹⁴⁴	275d	β 0.35
Pr ¹⁴³	13.8d	β 0.83
Nd ¹⁴⁷	11.0d	β 0.9 γ 0.58
Sm ¹⁵³	47h	β 0.78 γ 0.61
Eu ¹⁵²	$\sim 5y$	β 0.75
Eu ¹⁵⁴	$\sim 7y$	β 1.0 γ 1.23
Gd ¹⁵³	$> 70d$	γ 0.1
Tb ¹⁶⁰	77d	β 0.88 γ 1.15
Ho ¹⁶⁶	27.5h	β 1.8
Er ¹⁶⁹	9.4d	β 0.33
Tm ¹⁷⁰	127d	β 0.98
Yb ¹⁷⁵	99h	β 0.5 γ 0.35
Lu ¹⁷⁷	6.6d	β 0.47

Most analytical work with radioactive isotopes involves handling less than 1 millicurie of activity. At such a level, normal, orderly, analytical laboratory arrangements are adequate except for storage facilities and the inclusion of some easily observed precautions and special techniques.

The general principle of isotope tracer techniques is simple. If the assumption is made that the labelled compound behaves exactly like the unlabelled compound in every way, then, whatever information, quantitative or qualitative, is obtained concerning the labelled compound applies also to the unlabelled compound. Quantitative information concerning the labelled compound is derived from the ratio of its activity before introduction into the experimental mixture to that in samples obtained from the experiment. For example, in mixture of elements *A* and *B* it is desired to determine the efficacy of a process employed to separate *A* from *B*. Some radioactive isotope *A** is then added in amount equivalent to an activity of e.g. 20,000

cpm. The separation process is applied. If then the total activity of the separated A is only 10,000 cpm, it is evident that, taking into account the half life of the isotope, and the length of time that the separation has taken, the process for separating A from B has only been 50 per cent effective.

Probably the most important analytical application of 'tracers' is the isotope dilution effect. This is particularly useful for the determination of a constituent in a mixture of such complexity that it is either impossible or extremely difficult to separate the desired constituent from interfering substances quantitatively and without loss. By this technique a value for the constituent to be determined may be obtained if only a fraction of it can be isolated in a pure condition. Thus, we desire to determine the weight (x) of a substance (' a ') which is contained in a definite weight (' g ') of a sample admixed with difficultly soluble ' b ' and ' c '. To the solution of the known weight of a mixture sample is added a known weight ' y ' of a^* (radioactive ' a ') of known specific activity S_o (cpm/g). After this addition we isolate a small amount of pure ' a ' (containing a^*) and determine its weight and specific activity ' S_f '. The content of ' a ' in the original sample may then be resolved by

$$x = y(S_o/S_f - 1)$$

Thus, by determining the specific activity and weight of the tracer to be added, and the specific activity of the isolated material — which must however be in pure form — the weight of the latter in the sample may be determined without the need for a quantitative method of separation. Where the activity of the tracer is such that only a minute amount, less than a microgram, needs to be added to the solution to give a good count rate, the calculation becomes even simpler. Knowing the overall activity added and the activity of the pure fraction obtained, the percentage of ' a ' then becomes:

$$\frac{x \cdot A_o / A_r \cdot 100}{g}$$

where x is the weight of ' a ' recovered

A_o and A_r are original and recovered activities

g is the original sample weight.

In some analyses it is necessary to work with tracer material of unknown specific activity. Assume it is desired to determine the

number of grams 'x' of an element in a complex mixture and we have a tracer of unknown specific activity but containing a known total activity A cpm. This quantity, which is negligible in weight when compared with that of 'x', is added to the sample and 'z' g of the pure element isolated with an activity of B cpm, the amount of 'x' in the sample then becomes $x = z A/B$.

It was observed many years ago that radioactive elements at extremely low concentrations behave in some solutions more like colloids than true solutes. It must be remembered, therefore, that colloid adsorption phenomena may occur on container surfaces, filter paper, etc., and at low concentrations may introduce a source of error. The same effects undoubtedly occur in work at ordinary concentrations but then the amount of material involved represents such a small fraction of the total that these effects are negligible.

Where the quantity of a rare earth is small, or where small amounts of mixed rare earths are being sought by tracer techniques, it is possible to utilize co-precipitation procedures employing 'carrier' precipitates or by use of radioactive precipitants, e.g. C^{14} in oxalic acid for precipitating the oxalate, P^{32} in a phosphate precipitant, and F^{18} in fluoride precipitation.

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APPENDIXES

APPENDIX I

GEOCHEMICAL ASSOCIATIONS

THE MOST recent data on abundances of rare earths presented by Suess and Urey⁽¹⁾ are given in Table I-1 and the consensus is that the abundance ratios have undergone little, if any variation since the beginning of time. The odd-even rule is well displayed as is the general tendency to increased rarity with increasing atomic number.

The rare earths are strongly lithophile and in general associated with igneous rocks. A minor degree of differentiation of rare earths is observed with magmatic habitat, the lighter lanthanons tending to be associated with basic rocks and the heavy earths with the silicic igneous rocks. The general inability of the rare earths to replace Mg^{2+} and Fe^{2+} in magma leads to their concentration in pegmatites.

In general, mineral associations are largely dependent upon similarities in ionic sizes and ionization potentials⁽²⁾ and interesting relationships are noted involving titanium, tantalum and niobium, scandium, yttrium and thorium. In minerals of the euxenite-samarite-kite-polycrase type, the ratio of heavy:light rare earths, appears to be in direct proportion to TiO_2/R_2O_5 . Scandium is associated only with relatively high contents of ytterbium⁽³⁾ and this appears to hold even when, in metamicts, the normal relationship of heavy:light lanthanons is disturbed⁽⁴⁾. According to Goldschmidt and Peters⁽⁵⁾ we may expect scandium to be associated with minerals of magnesium or bivalent iron but not regularly with zirconium and hafnium, although these latter elements may be found with scandium. All magmatic olivines have been found to contain scandium in detectable quantities but scandium is not found in the alumina minerals of eruptive rocks. Scandium is not found in unaltered feldspars or nephelines but pyroxenes and garnets frequently are rich in the element. The occurrence of scandium in some wolframites is due to its displacement of Fe^{2+} and Mn^{2+} , but conversely little association is found with scheelite. Some cassiterites have been found to contain scandium but it is not clear whether this is a direct occurrence or attributable to co-mingled wolframite.

In typical rare earth minerals seven types of mineral compositions have been found to occur⁽⁵⁾ in which complete assemblage is shown by apatite ($Ce > Nd$) and yttrifluorite ($Ce = Nd$) and selective assemblage by thalenite ($Dy > Er > Yb > Gd$), thortveitite ($Yb + Sc$ greatly predominate) allanite-monazite ($Ce > Nd > La > Pr > Sm$) xenotime ($Yb = Er > Dy > Gd$) and wiikite ($Yb > Dy > Er = Gd = Sm > Nd$). An unusual distribution was found for davidite⁽⁶⁾ but it would now seem that in such metamicts, variation from conventional behaviour can be expected.

TABLE I-1. ATOMIC ABUNDANCES OF
RARE EARTH ELEMENTS
(relative to $Si = 1 \times 10^6$)^a

Sc	28.0	Gd	0.684
Y	8.9	Tb	0.096
La	2.00	Dy	0.556
Ce	2.26	Ho	0.118
Pr	0.40	Er	0.316
Nd	1.44	Tm	0.032
Pm	0	Yb	0.220
Sm	0.664	Lu	0.050
Eu	1.87		

Because of its great abundance and economic value, monazite, and the rare earth relationships therein have been much studied and Wylie has suggested⁽⁷⁾ that a high heavy lanthanon content is associated with a lower lanthanum content. In general, agreement is found with Murata *et al.*⁽⁸⁾ that the sum $La + Nd$ is very nearly constant at 42 at. per cent, Pr is nearly constant at 5 at. per cent and $Ce + Sm + Gd + Y$ is very nearly constant at 53 at. per cent other than this, little evidence is found for inter-element relationship.

In cerium earth mineral species as a whole, the sum of atomic percentages for La , Ce and Pr falls between 58 and 92. Monazites, cerites and allanites cover the whole range but bastnaesites are restricted to summation values between 80–92 per cent. Cerium earth minerals from alkali rocks are all characterized by summation values greater than 80 at. per cent.

The summation rules are of some value to the analyst since if, for example, lanthanum or neodymium are determined, a good approximation can be obtained for the content of the other element by simple

addition. Further, any gross violation of the 5 per cent rule for Pr would immediately suggest further examination.

It is to be hoped that further systematic studies of rare earth minerals will be made, further to aid rationalization of their compositions.

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APPENDIX II

CONVERSION FACTORS

Unbracketed figures given are for conversion of metal to the corresponding anhydrous compound. Figures in parentheses are reciprocals and for the reverse conversion.

Element	At. Wt.	Oxide	Hydroxide	Carbonate	Oxalate	Fluoride	Chloride	Nitrate	Sulphate
Sc	45.1	1.532 (0.6527)	2.131 (0.4693)	2.996 (0.3338)	3.927 (0.2546)	2.264 (0.4417)	3.361 (0.2975)	5.124 (0.1952)	4.195 (0.2384)
Y	88.92	1.270 (0.7874)	1.574 (0.6353)	2.012 (0.4970)	2.484 (0.4026)	1.641 (0.6094)	2.198 (0.4550)	3.092 (0.3234)	2.620 (0.3817)
La	138.92	1.173 (0.8525)	1.367 (0.7315)	1.648 (0.6068)	1.950 (0.5128)	1.410 (0.7092)	1.767 (0.5639)	2.339 (0.4275)	2.037 (0.4909)
Ce (3+)	140.13	1.171 (0.8540)	1.364 (0.7331)	1.642 (0.6090)	1.942 (0.5149)	1.407 (0.7107)	1.760 (0.5682)	2.327 (0.4297)	2.028 (0.4931)
Ce (4+)		1.228 (0.8143)	1.485 (0.6734)	1.856 (0.5388)	— (0.6485)	1.542 (0.6485)	— (0.6485)	2.770 (0.3610)	2.371 (0.4218)
Pr (3+)	140.92	1.170 (0.8547)	1.362 (0.7342)	1.639 (0.6101)	1.937 (0.5163)	1.404 (0.7123)	1.756 (0.5695)	2.320 (0.4310)	2.022 (0.4946)
Pr (4+)		1.227 (0.8150)	— (0.8150)	— (0.8150)	— (0.6498)	1.539 (0.6498)	— (0.6498)	— (0.6498)	— (0.6498)
Nd	144.27	1.166 (0.8576)	1.354 (0.7386)	1.624 (0.6158)	1.915 (0.5222)	1.395 (0.7168)	1.738 (0.5754)	2.289 (0.4369)	1.999 (0.5003)
Sm (3+)	150.43	1.160 (0.8621)	1.339 (0.7468)	1.598 (0.6258)	1.877 (0.5328)	1.379 (0.7252)	1.708 (0.5855)	2.236 (0.4472)	1.958 (0.5102)
Sm (2+)		1.106 (0.9042)	— (0.9042)	— (0.9042)	— (0.7981)	1.253 (0.7981)	1.472 (0.6793)	2.277 (0.4392)	2.277 (0.4392)
Eu (3+)	152.0	1.158 (0.8636)	1.336 (0.7485)	1.592 (0.6281)	1.868 (0.5353)	1.375 (0.7273)	1.701 (0.5879)	2.224 (0.4496)	1.948 (0.5133)
Eu (2+)		1.105 (0.9050)	— (0.9050)	— (0.9050)	— (0.8000)	1.250 (0.8000)	1.467 (0.6817)	— (0.6817)	1.632 (0.6127)
Gd	156.9	1.153 (0.8673)	1.325 (0.7547)	1.574 (0.6353)	1.841 (0.5432)	1.363 (0.7337)	1.679 (0.5956)	2.185 (0.4577)	1.918 (0.5214)
Tb (3+)	159.2	1.151 (0.8688)	1.320 (0.7576)	1.565 (0.6390)	1.829 (0.5467)	1.358 (0.7364)	1.669 (0.5992)	2.168 (0.4613)	1.905 (0.5249)
Tb (4+)		1.201 (0.8326)	— (0.8326)	— (0.8326)	— (0.6770)	1.477 (0.6770)	— (0.6770)	— (0.6770)	— (0.6770)
Dy	162.46	1.148 (0.8711)	1.314 (0.7610)	1.554 (0.6435)	1.813 (0.5516)	1.351 (0.7402)	1.652 (0.6053)	2.145 (0.4662)	1.887 (0.5299)
Ho	164.94	1.146 (0.8726)	1.309 (0.7639)	1.546 (0.6468)	1.800 (0.5556)	1.346 (0.7429)	1.646 (0.6075)	2.128 (0.4699)	1.874 (0.5336)
Er	167.2	1.144 (0.8741)	1.305 (0.7663)	1.538 (0.6502)	1.789 (0.5590)	1.341 (0.7457)	1.637 (0.6109)	2.112 (0.4735)	1.862 (0.5371)
Tm	169.4	1.142 (0.8757)	1.301 (0.7686)	1.531 (0.6532)	1.779 (0.5621)	1.336 (0.7485)	1.629 (0.6139)	2.098 (0.4766)	1.851 (0.5402)
Yb (3+)	173.04	1.139 (0.8780)	1.295 (0.772)	1.520 (0.6579)	1.763 (0.5672)	1.329 (0.7524)	1.615 (0.6192)	2.075 (0.4819)	1.833 (0.5456)
Yb (2+)		1.092 (0.9158)	— (0.9158)	— (0.9158)	— (0.8197)	1.220 (0.8197)	1.410 (0.7092)	— (0.7092)	1.555 (0.6431)
Lu	174.99	1.137 (0.8795)	1.291 (0.7746)	1.514 (0.6605)	1.754 (0.5701)	1.326 (0.7541)	1.609 (0.6215)	2.063 (0.4847)	1.823 (0.5485)

APPENDIX III

POLAROGRAPHY

THE ONLY rare earth elements which can be determined satisfactorily by means of the polarograph are europium and ytterbium. Polarographic procedures are eminently suitable for following the formation of complex rare earth ions and determining stability constants of the complexes formed⁽¹⁾ but direct, analytical, polarography of the rare earth elements other than europium and ytterbium is indeterminate. Noddack and Brukl⁽²⁾ determined the reduction potentials of rare earth sulphate solutions and claimed two-step reduction for all members of the series. This, however, has been discredited except for those lanthanons known to give rise to bivalent ions, i.e. samarium, europium and ytterbium⁽³⁾ — all others undergo a three-electron reduction directly to the metallic state. Polarographic determination of cerium in complexed form has been suggested⁽⁴⁾, but the procedures proposed offer no advantages over other, conventional, oxidation-reduction procedures.

Table III-1 lists electrode and redox potentials of the rare earth ions. Half wave potential values for $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$, and $\text{Yb}^{3+} \rightarrow \text{Yb}^{2+}$ are seen to be quite well defined but that for samarium reduction, lying in the region of metal deposition, is unsuitable for analysis.

Holleck⁽⁵⁾ proposed an indirect polarographic method for the determination of europium involving the addition of a known concentration of zinc to the rare earth solution followed by calculation of the europium concentration from the relative wave heights obtained for europium and zinc. As Laitinen and Taebel⁽⁶⁾ pointed out, however, the procedure suggested will yield only approximate data since it is tacitly assumed that the zinc and europium ions have equal diffusion coefficients — that for europium can be expected to be somewhat lower than that for zinc.

Laitinen and Taebel found that although the $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ electrode system is not strictly reversible, its deviation from reversible behaviour is too small to be considered influential in analytical procedures. The E_1 value obtained was -0.425 V, in close agreement with

the value of -0.43 V for the normal potential reported by McCoy⁽⁷⁾; McCoy's work was, however, based upon ionic concentrations rather than activities.

For ytterbium reduction at the dropping mercury electrode, Laitinen and Taebel found the half wave potential to be -1.415 V (*versus* saturated calomel electrode) or -1.169 V (*versus* normal hydrogen electrode).

TABLE III-1. ELECTRODE AND HALF-WAVE POTENTIALS

	E_0 V	$E_{\frac{1}{2}}$ V
Sc $\rightarrow$ Sc ³⁺ + 3e ⁻	2.08	-1.88
Y $\rightarrow$ Y ³⁺ + 3e ⁻	2.37	
La $\rightarrow$ La ³⁺ + 3e ⁻	2.52	
Ce $\rightarrow$ Ce ³⁺ + 3e ⁻	2.48	
Ce ³⁺ $\rightarrow$ Ce ⁴⁺ + e ⁻	-1.61	-1.96
Pr $\rightarrow$ Pr ³⁺ + 3e ⁻	2.47	
Pr ³⁺ $\rightarrow$ Pr ⁴⁺ + e ⁻	-1.60	
Nd $\rightarrow$ Nd ³⁺ + 3e ⁻	2.44	
Pm $\rightarrow$ Pm ³⁺ + 3e ⁻	2.42	-2.30
Sm $\rightarrow$ Sm ³⁺ + 3e ⁻	2.41	
Sm ²⁺ $\rightarrow$ Sm ³⁺ + 3e ⁻	1.72	
Eu $\rightarrow$ Eu ³⁺ + e ⁻	2.41	
Eu ²⁺ $\rightarrow$ Eu ³⁺ + 3e ⁻	0.43	-0.671
Gd $\rightarrow$ Gd ³⁺ + 3e ⁻	2.40	
Tb $\rightarrow$ Tb ³⁺ + 3e ⁻	2.39	
Dy $\rightarrow$ Dy ³⁺ + 3e ⁻	2.35	
Ho $\rightarrow$ Ho ³⁺ + 3e ⁻	2.32	1.415
Er $\rightarrow$ Er ³⁺ + 3e ⁻	2.30	
Tm $\rightarrow$ Tm ³⁺ + 3e ⁻	2.28	
Yb $\rightarrow$ Yb ³⁺ + 3e ⁻	2.27	
Yb ²⁺ $\rightarrow$ Yb ³⁺ + e ⁻	1.15	
Lu $\rightarrow$ Lu ³⁺ + 3e ⁻	2.25	

Accuracies of 0.01 per cent can be obtained in polarographic analysis of europium and ytterbium using ammonium chloride (0.1 N) as the supporting electrolyte and the derivative technique of Pomeroy *et al.*⁽⁸⁾. Powell⁽⁹⁾ considers the method best applied by using the Cambridge polarograph with the Univector attachment, and the rare earths in a 4 per cent solution (based on oxide content) of the neutral chlorides in 0.1 N ammonium chloride. Powell has found the europium peak to occur at -0.9 V and that for ytterbium at -1.6 V. The average slope of the logarithmic plot of potential

versus current is 0.079 V for europium and 0.66 V for ytterbium. If standards are determined simultaneously with the samples an accuracy of better than 0.002 per cent is claimed⁽⁹⁾.

The general procedure, based upon Laitinen and Taebel (*loc. cit.*), is as follows:

Dissolve approximately 2 g oxide in 15 ml 6 N hydrochloric acid and dilute to 100 ml in a volumetric flask. Transfer 10 ml to a 50 ml flask and add one drop methyl red indicator solution. Titrate the solution with 0.5 N NH_4OH using, as a colour comparison, 25 ml 0.1 N NH_4Cl containing a drop of methyl red solution. Add then sufficient 1 N ammonium chloride to bring its concentration to 0.1 N after dilution to 50 ml. Determine the current-voltage curve in the usual way.

Since europium occurs only in very low concentrations in natural rare earth minerals, analytical beneficiation is usually involved prior to its determination in rare earth mixtures. This is readily achieved by single passage through a small cation exchange column, elution being effected by acetate solution, followed by treatment with sodium amalgam (Chapter IV). Since europium will, most commonly, be found in minerals of the lighter earths, the fractions first eluting from a cation exchange column charged with a light earth solution, will contain the europium. Elution, with 0.1 per cent ammonium acetate, should be carried to the point at which the pink colour of neodymium becomes prominent. The eluate to this point is concentrated and shaken with sodium amalgam. After separating the mercury and aqueous layers, europium is recovered from the amalgam with hydrochloric acid, the solution evaporated somewhat and treated as above.

The successful polarographic determination of ytterbium in rare earth mixtures depends upon obtaining well defined reduction waves in the presence of large concentrations of the other rare earths and a preliminary concentration to about 25 per cent is necessary to meet this requirement. Here again, adequate beneficiation may be achieved by passage through a short resin column, ytterbium concentrating in the first fractions. Elution is continued until strongly pink solutions are obtained indicating the presence of erbium. From this point the determination follows that indicated above for europium.

Because the reduction potentials of europium and ytterbium are widely separated no difficulty is encountered in determining these elements in the presence of each other. However, in determining the

diffusion current of ytterbium in such a mixture, care must be taken to correct for the decreasing diffusion current of europium with increasing negative potential. In practice, however, the analyst will be unlikely to meet with systems containing both europium and ytterbium in appreciable concentrations in the same sample. This could, however, derive from a mixture of reducible elements obtained by the amalgam — reduction extraction from e.g. davidite or similar metamict minerals.

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